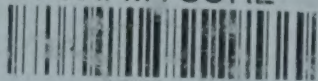


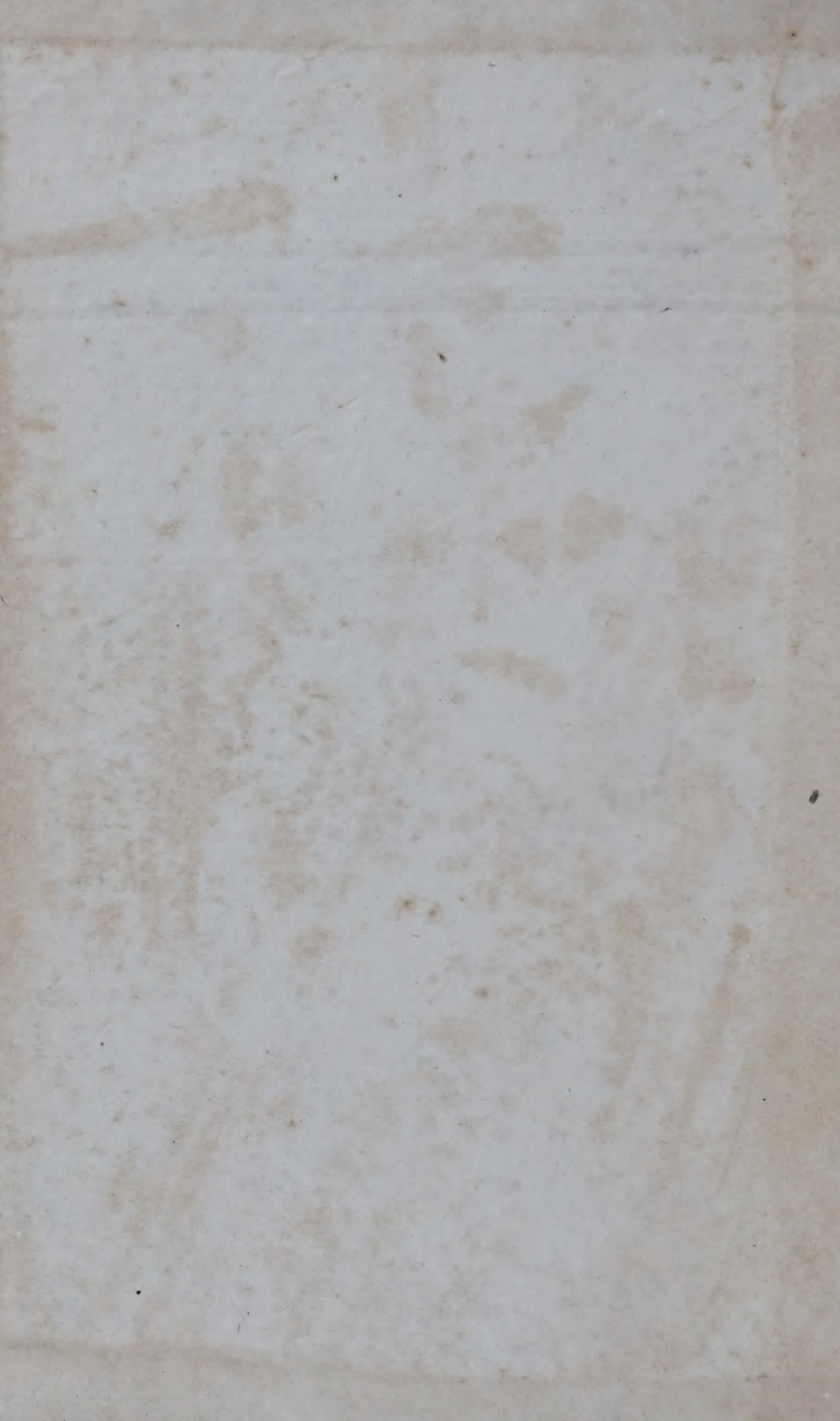
Chemical Industry of India.

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CHAPTER I.

**POSSIBILITIES OF CHEMICAL INDUSTRIES
IN INDIA.**

IT would be futile to match any industry more varied in character and wider in scope than the chemical industry. The prospects of very many existing industries in the country are vitally connected with those of the chemical industry. It is a key industry, its products being used in most other industries, in the textile industry, the leather industry, the paper industry, the glass and porcelain industry, the rubber industry, in the making of artificial silk, paints and varnishes, soap and candles, and in the purification of the mineral and vegetable oils. Some of the products of this industry form the basis of explosives which are of supreme importance for national defence in times of war. On the science of chemistry, more than on any other branch of organised knowledge, depend the material well-being and comfort of man.

The products of the chemical industry are exceedingly numerous and varied in character, but comparatively few come into the hands of the mass of the people for direct consumption, for it is often the case that the finished product, bye-product, or waste from one industry, becomes the raw material for another. It rarely happens that one manufacturer, starting with the raw materials found in nature, produces from them articles for popular use. Thus the chemical industries become a net-

tries in which the industry has reached a high level organisation. Manufacture of other chemicals for which there are natural facilities has also proved profitable.

In addition to these chemicals, drugs and extracts are manufactured on a small scale, but only in official medical stores and by a few private factories on an recognised standard of purity and strength.

SULPHURIC ACID—THE FIRST ESSENTIAL

For the successful development of chemical industries the first essential is to manufacture sulphuric acid at sufficiently low rates. To make its manufacture a technical success the bye-products must be taken into consideration and as little waste should be allowed as possible. It would appear that India is strangely backward in her consumption of sulphuric acid which is probably the most essential material in use in the chemical industry. Although nearly 20,000 tons of sulphuric acid are said to be made annually in India from imported sulphur, the demand for this chemical is small. India's consumption of this acid of 20,000 tons pales into insignificance in comparison with the figure of world consumption, 10,000,000 tons. If therefore the demand for sulphuric acid is taken as the chemical barometer of the industrial conditions, industrial activity in India seems to be in its infancy. In view of the expanding conditions of the manufacturing industries of India, however, the manufacture of sulphuric acid is of great importance.

INDIAN DEFICIENCY IN ALKALIES.

Next in importance to sulphuric acid comes the manufacture of alkalies such as soda carbonate, soda bicarbonate

bonate, caustic soda and caustic potash, ammonia, ammonium sulphate, etc. These are largely employed in manufacturing glass, paper and soap, in dyeing, mercerising, bleaching, sizing and finishing, for household washing purposes and a number of other industries. India is specially deficient as regards the manufacture of alkalies. The production of the acids has been almost sufficient to meet the demand in the country but huge imports of soda compounds every year only expose the weakness of the Indian chemical industries. Formerly India used to manufacture these alkalies from the efflorescence found in the soils of the Punjab, Hyderabad, Mysore, etc. but the crude method has failed against stronger foreign competition. Sources of alkali manufacture are not wanting in the country, e.g., salt occurs in abundance and can be decomposed by electrolytic process to yield caustic soda.

LINES OF DEVELOPMENT.

There is ample scope for enterprise in the inauguration and extension of chemical industries in India. The available raw materials would suffice to supply nearly all of India's requirements in acids, alkalies, salts and other chemicals, organic or inorganic.

It is interesting to record that under cover of war start has already been made in India for the manufacture of soda ash, bleaching powder, caustic soda, etc., on a small scale. Besides several concerns have under project the manufacture of sodium and potassium bichromate, acetic acid, oxalic acid, tannic acid and other acids and alkalies.

In the first instance industries which make use of Indian raw materials, now exported to other countries may be worked up into finished products. Alum salts, barytes, borax, gypsum, lime-stone, magnesite, phos-

phate of lime and ochres may also be more and more employed for the manufacture of heavy chemicals. The installation of plant for the recovery of by-products in coking has recently been undertaken but for the recovery of tar and ammonia only. The recovery of benzol and related products has so far not been attempted, nor has any thing been done to utilise the tar by re-distillation or other chemical treatment.

Given cheap electric energy India could also produce a large quantity of calcium carbide. Magnesium chloride which is an essential chemical in textile and paper industries as sizing material can also be prepared from bitter left after salt manufacture.

Indian saltpetre deposits need better care: investigations are necessary to find out a possible utilisation of the crude nitre and the refuse for the manufacture of other compounds of potassium or sodium; the large manufacture of salt from sea-water leaves considerable room for the isolation and purification of magnesium compounds; and similarly the mineral rock salt of the Punjab needs more thorough investigations for the separation of magnesium and potassium salts; the utilisation of the reh efflorescence even as a source of sodium compound is an unsolved problem; finally the large deposits of aluminous minerals, e.g., laterite and clays bid fair to an industry for the manufacture of aluminium or its salts. There is specially a wide scope for the manufacture of chemicals used in sizing, bleaching and dyeing of cotton goods.

There is also a great field for the manufacture of disinfectants and antiseptics. Disinfectants may be divided roughly into two groups, inorganic and organic disinfectants.

tants. The chief members of the first group are, sodium and potassium permanganate, bleaching powder, hypochlorite solutions and boracic acid, whilst in the second group we have formaldehyde, the chloramines and the acid constituents of coal tar, carbolic acid and the cresols.

Scientific agriculture insists upon the need for replacing in the soil the mineral constituents removed by the crops, if the yields per acre are to be maintained. The mineral constituents essential for plant growth are potash and nitrogenous compounds, lime and phosphates. India is essentially an agricultural country and it might be expected to use enormous quantities of fertilisers. In the planting districts, the great advantage to be gained by the systematic use of chemical has long been realised. The chief phosphatic fertilisers for such products as tea, coffee and rubber are: (a) bones in the form of bone-meal, (b) super-phosphates manufactured from bones and sulphuric acid or from the natural mineral phosphates and sulphuric acid and (c) basic slag obtained from the iron and steel works. The common nitrogenous artificial manures are: (a) ammonium sulphate, (2) salt-petre and nitre, (3) nitroline, (4) oilseed cakes, (5) nitrates, mainly calcium and ammonium, obtained from atmospheric nitrogen.

The possibility of manufacturing good fertilisers from rock phosphate is no less promising. Apatite, which is the technical name for rock phosphate is known to occur in many parts of India. There is considerable quantity of deposits in the Singbhum district which may be suitably utilised in the manufacture of superphosphate.

Manufacture of drugs and essential oils hold out great possibilities in India. Already a number of indi-

genous drugs have been put in the market and ever-increasing demand for them ensures good profits to the first comers.

CHEMICAL RESEARCH.

Nothing is of greater importance to the success of the chemical industry than an active programme of chemical research in all factories. Every factory which expects to go on and flourish in these days of keep competition and price-cutting should not shut its eyes to the imperative necessity of fostering research in bringing about improvement of the existing qualities, reduction in the prices of the products, elimination of the wastes in the diverse processes of manufacture, utilization of the bye-products which pile up in factories and even entail expenditure for their removal, and expansion of the range of their products by taking up new or allied manufactures. It should also be the aim of chemical research to standardise the products and examine or test them before they are placed in the market. It should also attempt to discover new processes of manufacture which will not only improve the quality but will also lower the cost of production.

Now-a-days almost in every country more and more attention is being paid to chemical research. If the advanced countries of the West, America and Japan still stand in need of chemical research, it is more so in the case of India which lags behind these countries and is much backward. India should make it a point to fall in line with them. The vast mineral, forest and agricultural resources of India cannot be exploited to their fullest extent unless opportunities are given to chemists for research. Every modern chemical industry, so to speak,

carries on its own research for investigation purposes and if India is to keep pace with modern conditions and to create its own industrial environments, it can adopt no better measure than the establishment of up-to-date laboratories in all chemical factories.

Stress should also be laid on the necessity of co-ordination between the manufacturers and research institutions. Encouragement should be given so that the research institutions as well as the manufacturers put their heads together to find out ways and means for better utilisation of the opportunities of research with a view to the rapid progress of the chemical industry in this country.

PRE-REQUISITES FOR SUCCESS.

India is late in the field of industrial chemicals. The Western countries, for example, started more than half a century ago and thus had the rare opportunity of specialising in the manufacture of the various lines of chemicals. For example, England is noted for its soda compounds which find market all over the world, the Germans have established a reputation of being the only manufacturers of genuine dye stuffs, Norway has made a name for carbide, and so on. It is therefore most necessary to have an idea of the industries which have any chance of flourishing in India.

It has been our purpose in the book to deal with manufacture of such articles which may be carried on with profit. It would be fruitless now to cover the whole ground of industrial chemistry and give manufacturing processes which will only be of academic value. The chemicals treated in this treatise have been classified under several heads such as acids and their derivatives, alkalies, organic compounds, miscellaneous compounds, etc., etc.

rials or, treating agents for other process industries. The importance of heavy chemicals, therefore, lies in the fact of their being essential for other industries like textiles, soap, rayon, fertilisers, glass, leather, paper, etc. and their consumption depends on the activity of these industries. Consequently there must be an all-round development of consumer industries to enable a sound heavy chemical industry to be established. The main heavy chemicals are, as generally understood, sulphuric and other mineral acids and related compounds, soda ash, caustic soda and fertilisers.

Again there has been in India very little development in electro-chemical industries except for one or two items. For want of these, India suffered considerably during the recent war. With the completion of the hydro-electric projects now being planned, abundant power will become available and it will be possible to establish many electro-chemical industries.

FINE CHEMICALS.

The Industrial Advisory Board Panel on Fine Chemicals, Drugs and Pharmaceuticals considers that the proper development of the fine chemicals and drugs industry leading to self-sufficiency would depend very much on working out a well-balanced and integrated plan for the production of heavy chemicals, coal distillation products, organic solvents, etc.

Among the heavy chemicals, the manufacture of three items, i.e., chloro-sulphuric acid, sodium, and chlorides of phosphorous, is very important. The production of intermediates from coal distillation products, such as aniline, acetanilide, chloro-benzene, phenol diethyl aniline, para-anisidine, para-nitrotoluene, phthalic acid and an-

hydride, etc., may be given the second order of precedence. Among solvents, India produces ethyl alcohol in good quantities at competitive prices. Acetone is being produced at one of the ordnance factories. If the production of acetone in the factory, where it is not required for making explosives, is kept up, the needs of the drug industry, it is believed, will be met to a great extent. Immediate arrangements should be made, in the meanwhile, for the manufacture of other solvents, such as acetic acid, butyl and amyl alcohols, and also in respect of ethylene oxide, which is a valuable intermediate. The Panel has also stressed the need for taking immediate steps for the manufacture of the requisite quantities of lactose, thourea, and guanidine nitrate, the first of which is required for the manufacture of penicillin and the second and third for the manufacture of sulpha drugs.

The immediate manufacture of all the above chemicals can be started only if a practical programme is chalked out and adhered to by the Government. According to the suggestion put forward by the Panel the most practical way to establish the fine chemicals and drugs industry would appear to be to decide first on the minimum number of drugs and fine chemicals essential for the country. The production of these essential drugs should be taken up at once without waiting for the production of basic chemicals already available and importing those not available here until national resources are fully developed.

DRUGS.

The immediate production of two types of drugs has been suggested by the Industrial Panel on Fine Chemicals and Drugs, namely, those which are essential for

various districts in the Indo-Gangetic tract, especially in the Bihar section, chiefly Gaya, Tirhut, Saran and Champaran. Commercial Saltpetre is also obtained in many other parts though to a less extent e.g., Allahabad, Benares, Kanpur, Ghazipur in the U. P., Coimbatore, Kistna, Madura, Salem, Trichinopoly, Vellore in Madras, Bhinmal and Jwargarh in Central India, as also in the Punjab and Kashmir. It is obtained in a crude form and unless it is refined it cannot be put on the market. The process is carried on in Northern India e.g., in the Punjab, North-West Frontier Provinces, United Provinces and Bihar.

BAUXITE.

Bauxite, the chief source of manufacturing aluminium, is found in working quantities in Khairā District, Jubbulpore, Ranchi District, Kalahandi State and the Palam Hills. It occurs in the Bihar plateau in the Balaghat District, in the vicinity of Katni and in the Mandla District. Large deposits also occur in the Bombay Presidency particularly in the Belgaum District and in Kolhapur State. The manufacture of aluminium was first pioneered in Madras and subsequently the industry got a stronghold over South India.

GYPSUM.

In an impure state gypsum is met with abundantly near Trichinopoly. In mass formation it is found in the clays of Chingleput. It is found in the Jhelum District and the Bikaner and Jodhpur District. Crystals of selenite are fairly prevalent near Nellore. In Bombay, selenite occurs in the marine deposits near the city, also in Kathiawar and in some parts of the Deccan. Gypsum of excellent quality is found in Cutch and also in Sind.

A bed of gypsum has been worked in Rajputana near Jodhpur and in Bikaner.

In the Punjab the mineral occurs in some places in the Jammu district. The Kohat district contains gypsum in great abundance. Associated with rock salt it occurs in enormous quantity in the Salt Range. The Spiti Valley has gypsum of a snowy whiteness. Deposits have been discovered in some places in the United Provinces.

Gypsum is generally regarded as a manure of considerable worth, especially for leguminous crops and for certain soils. The next most important use for gypsum is the numerous methods of utilising plaster of Paris. It is the hydrous form of calcium sulphate which parts with some of its water on calcination. It is then known as plaster of Paris.

BORAX.

Properly speaking, borax is an indigenous sodium borate found, along with common salt, on the shores of certain lakes in Tibet and in the neighbourhood of the Indian frontier. Borax is deposited with sulphur by hot springs in the Puga Valley of Ladakh, Kashmir. From there the local area of occurrence extends to the lakes of Budokh.

The supply of crude borax is admitted into the country by Kulu and is refined at Sultanpur. Therefrom it is consigned to Simla or Jagadhri and thence to the plains. Smaller quantities from this same source also find their way through Chamba to Nurpur or to Kashmir and Lahore. Tibetan borax enters India across the frontier of the United Provinces. It is purchased by Indian merchants from Bhotia traders at Ramnagar, where it is refined. The industrial applica-

The chief groups of rocks or materials that afford lime in India have been divided into three classes; (1) Lime-stones; (2) dolomite; (3) miliolite, etc.

The sources of lime and limestone from the point of view of commercial importance are: (1) Sutna in Rev and at Katni in the Jubbulpore district; (2) In Sylh along the foot of the Khasia and Jaintia Hills; (3) The lower Vidhyan limestone near Rohtasgarh is quarried to a small extent while good lime is made from the deposits at Bisra, in the Singbhum district; (4) Along the foot of the Himalayas, boulders of limestone are collected and burnt in large quantities; (5) A band of cream-coloured marble has been reported from the Andamans which may prove of economic importance.

Large quantities of lime are made in various parts of India from highly calcareous surface soil. This lime when mixed with proper proportions of sand makes most excellent mortar. For example, kankar is the chief source of lime in Upper India. It even yields an excellent and somewhat hydraulic cement.

All over India shells are burnt for lime. Deposits of shells, whenever met with, are regularly utilised as sources of lime. The prosperous Portland cement manufacture of South India is directly traceable to them.

On analysis it has been found that while the proportion of lime in lime-stone kankar is variable, that of shell preserves a uniform high average. As a manure lime plays an important part, specially for soils rich in organic matter. But by far the most important use of lime is as mortar, a cement which consists of lime, sand and water.

COPPER.

Copper mines occur in the vicinity of Ghatsila in the Singbhum district in Bihar where the ores are smelted

Copper ores are also obtained in the Nellore district of the Madras Presidency and in Mysore State. Many attempts have been made in the last fifty years to exploit the copper deposits of Chota-Nagpur. The matt was previously exported to Hamburg for further treatment.

GOLD.

India stands seventh amongst the gold-producing countries of the world. The bulk of the gold is obtained from the Kolar Gold Field in the Mysore State. The Hyderabad State and the Anantapur district of the Madras Presidency also produce a small amount. Gold is obtained from the beds of the Subarnarekha in Bengal in small quantities.

IRON ORE.

Good deposits of iron ore exist in many parts of India, such as Singhbhum, Mayurbhanj, Gua, Mysore and to a small extent in the Madras Presidency. As, however, deposits of coal necessary for working these sources of iron were seldom close at hand, they were neglected until quite recently. Now there are several companies interested in utilising these resources.

MANGANESE ORE.

Manganese ore is found widely distributed over India. The principal areas where it occurs are the Central Provinces, the Vizagapatam and Bellary districts and the Andur State in the Madras Presidency, the Panch Mahal district in Bombay Presidency, the Mysore State, Jabua in Central India and in Bihar and Orissa. Occurrences of manganese ore have been taken advantage of at the works of the three principal Indian iron and steel

from which the ore was distilled, contain varying quantities of zinc and lead.

TIN.

Cassiterite has been found in four localities in the Archaean rocks of the Hazaribagh district, Bihar and Orissa. At Simratari it occurs in lenticles of granite enclosed in mica schist; near Pihira, in a dyke of lepidolite granite, and at Chappatand in a granulite. All these places lie in the mica belt around Gawan. A thin layer of cassiterite-bearing granulite, in a much thicker band of microcline granulite, at Nurunga, near Parasnath, has attracted the attention of miners from 1867 onwards, but the amount of tin ore which it has yielded is quite insignificant. Indeed, all these occurrences in India proper appear to be of more scientific interest than practical importance.

PURITY.

Moreover, all the minerals of which the supplies are adequate are found in quality sufficiently pure for them to be utilized in the chemical industry, but the metallic sulphates and the phosphates can only be used after suitable treatment which is very expensive frequently.

It is only proper that organised efforts should be made to utilise these raw materials. Many of our industries, such as the manufacture of soap, glass, leather, drugs and textile fabrics (to name only a very few of the important ones) are now being hindered by the want of acids, alkalis and other chemicals which are required in large quantities at low prices. While a handicap is thus placed on the development of many home industries, large quantities of minerals (which form the raw materials for the

making of chemicals) are exported out of India at nominal values to be brought back as finished products to be obtained only at high prices by our manufacturers. Such a situation obviously means a great loss of wealth to our country. The loss is both positive and potential—the latter because the high cost of imported chemicals prevents the expansion of some of the home industries.

INDIA'S DEFICIENCY.

Hence considered from the point of view of raw materials India is not unfavourably situated. The only raw material not available in the country is sulphur which is the main source of sulphuric acid, the very first essential in the chemical industry. But it should be pointed out that in this respect India is at no disadvantage as compared with most other countries, since Italy, the United States and Japan are the only countries having considerable deposits of sulphur. It may be quite possible to manufacture sulphuric acid from substances other than sulphur. Among alternative sources the most important perhaps are zinc concentrates and gypsum. From each ton of these zinc concentrates we may obtain on smelting about one ton of chamber sulphuric acid as a bye-product. Then again substantial deposits of copper discovered in Singhbhum may prove a fruitful source of sulphuric acid. Hence so to speak the absence of an indigenous source of sulphur for the manufacture of sulphuric acid is not perhaps so serious a factor as it might appear.

SUCTION FILTER.

When both the filtrate and the precipitate are to be retained use is generally made of suction filters. This essentially consists of a box arranged so that the lower section is connected with the vacuum pump and over the perforated bottom is placed the canvas or other filtering medium.

EVAPORATION.

By the evaporation it is meant a process for the conversion of a fluid into vapour by means of heat, diminished atmospheric pressure, or exposure to a dry atmosphere. Evaporation is a most common process met in industrial chemistry and is taken recourse to:

(1) To separate volatile fluids from other bodies which are either fixed or less volatile. This process is better known as distillation.

(2) To recover solid bodies from their solutions, as in the preparation of extracts, chemical salts, etc.

(3) To strengthen or concentrate a solution by the expulsion of some of the fluid matter that form the menstruum.

(4) To purify liquids by the dissipation of the volatile matters which may contaminate them.

Evaporation may occur: (1) spontaneously; (2) by direct heat; (3) by indirect heat; (4) with the help of steam-jacketed kettles; (5) under reduced pressure; (6) with vacuum pans.

To evaporate a fluid spontaneously, the fluid should be exposed to the atmosphere in an open or partially open pan at the atmospheric temperature, i.e., no direct or indirect heat is applied to the pan. As the rate of evaporation mostly depends upon the extent of the surface, it

follows that shallow vessels with big surface area are most suitable for evaporation. For quickness of evaporation, the pan should be placed in a dry place where there is a constant current of dry air. The process is necessarily slow.

EVAPORATION BY DIRECT HEAT.

Evaporation may be conducted by the application of direct heat. The pan, in this case may either be of the open or closed type but in the latter case there should be outlets for the escape of the emitting gas. The pan is placed directly on the furnace which may be charged with coal or may be operated by gas or electric power. In this case the flame plays directly on the bottom of the pan.

In this case the evaporation is rapid and unless proper care is taken to agitate the whole mass, there is every chance of the whole thing being spoilt.

In some cases the flames or hot gases are made to pass over the surface of the liquid. In this case, however, the dust and ashes are likely to fall in the pan and may contaminate the product. This method can only be adopted in cases where the manufacturers do not insist on securing pure products. Again in this case the object may get injured due to over-heating.

EVAPORATION BY INDIRECT HEAT.

In this case the fluid is not allowed to come in direct contact with the source of heat. The evaporation is conducted on water-bath or sand-bath or with steam. This method is adopted when the composition of the fluid is rather delicate and the ingredients contained are likely to undergo decomposition on exposure to direct heat and the liquid is contained in a wooden cask.

In heating by water-bath, the arrangement of the pan should be such that the lower portion of the pan is in direct contact with water contained in another vessel which may be heated over an open furnace. The water in the vessel may be heated by steam.

Heating on water-bath is a dilatory process and is also very tedious. Elaborate arrangements are therefore made by the chemical factories. Steam is most convenient to handle and is therefore utilised in evaporation. The process consists in having a circulation of steam through coils of pipes arranged inside a vessel, especially when it happens to be a wooden vat. Pressure at which steam may be introduced is a deciding factor in evaporation. High pressure is generally accompanied with low evaporation.

Another method of utilising steam in evaporation is to use kettles constructed of copper or cast iron and provided with mechanical stirrers and fitted with a jacket surrounding almost the lower half of the kettle. Steam is made to pass through the jacket and the portions that condense are allowed to escape through an exit pipe. When no more condensation takes place, the exit pipe is closed and dry steam is allowed into the kettle through the inner pipe. The circulation of steam is so regulated as to attain the suitable temperature for evaporation.

EVAPORATION UNDER REDUCED PRESSURE.

As already referred to evaporation of fluids materially depends upon the atmospheric pressure to which it is subjected. Under heavy pressure, the evaporation is a very slow process while under reduced pressure the evaporation goes on briskly. This physical principle is made application of during evaporation. For this purpose special apparatus has been devised where the pressure is automatically

reduced with the result that the evaporation goes on steadily though there is no rise in temperature. The apparatus generally goes by the name of vacuum pans.

The pans may be either of simple effect or multiple effect type. The latter usually consists of three or four vacuum pans, so arranged that the steam of the first pan passes through the coil or jacket of the next pan and the steam generated in the second serves to heat the liquid in the third. The vacuum maintained in each of these pans increases as it approaches the pump for the reason that condensations play a quite important part in producing reduced pressure. The pan having the highest temperature has the least vacuum and vice versa. Usually a set of three pans are used at a time but sometimes four or more are used together.

LIXIVIATION.

The process of lixiviation separates water-soluble material from insoluble or less soluble material. The substance to be treated with water may be suspended in big baskets or placed in tanks provided with perforated false bottoms. The solution being denser than water sinks to the bottom and may be removed. The material is usually submitted to a systematic treatment with water in such a manner that the pure water first comes in contact with the nearly exhausted substance, and then with the less exhausted in another tank, and so on until it reaches the last tank, and so on until it reaches the last tank containing the fresh material. Such a series of tanks is known as a battery. The term extraction is generally used when solvents other than water are employed. It is possible to extract several substances from the original raw material by the successive use of several solvents such as water, alcohol, ether and naphtha.

CRYSTALLISATION.

Crystals are geometric solids which form when a compound separates from its concentrated solution. The solubility of most substances increases as the temperature of the solvent, usually water, is raised. A limit may be reached, however, for every temperature when no more will dissolve and the solution is said to be saturated. If the temperature be now decreased, crystals of the substance will separate and these crystals, though formed in an impure mother liquor, may be quite pure. By evaporation or concentration of the mother liquor more crystals will result which however will be less pure than the first crop. Thus this operation may be continued until the impurities accumulating in the liquor become so great that the crystals will enclose a large amount of foreign matter. This difficulty may be prevented to a certain extent by stirring the solution while crystallisation takes place and thereby causing the separation of very small crystals or crystal meal which can then be washed so as to reduce adherent impurities.

FRACTIONAL CRYSTALLISATION.

Crystals may be further purified by several successive re-crystallisations. This method is for the separation of substances mixed in a solution but it is obvious it will not be possible to separate isomorphous substances or those crystallising in the same system. In such a case reaction upon the solution must so change the chemical composition of one of the substances that separation by crystallisation becomes possible.

CALCINATION.

Calcination consists in strongly heating a substance in suitable turnaces to drive off moisture or some volatile

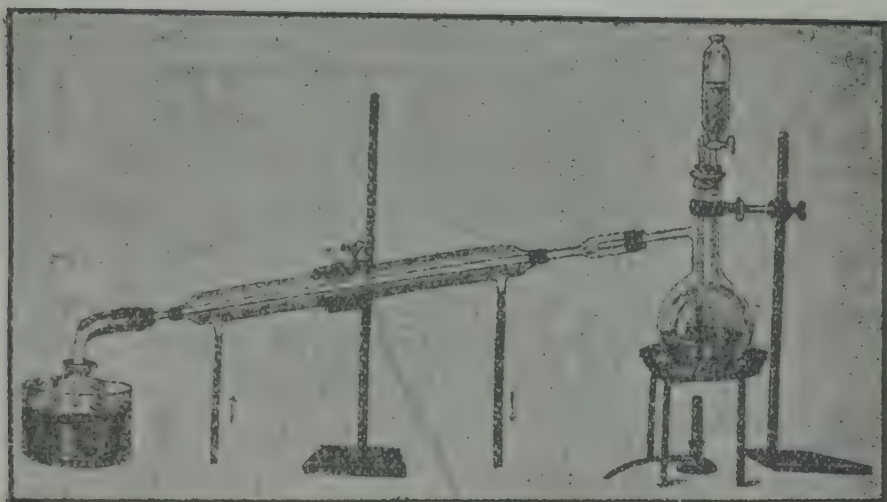


FIG. 1. DISTILLING APPARATUS.

[Page 33.



constituent or to cause a chemical action such as oxidation or reduction. The substance however is not heated to its fusing point. This operation is sometimes known as roasting.

DISTILLATION.

Distillation consists in the evaporation and subsequent condensation of the vapour of liquids. The substance operated upon is heated in a closed vessel (retort still) and thereby wholly or partially converted into vapour, which vapour is then condensed, by the application of cold, in another apparatus (the condenser) (Fig. 1) connected with the vessel and allowed to collect in a third portion of the apparatus called a receiver. The general object of distillation is to separate one substance from others of different degrees of volatility with which it may be mixed. The theory and successful execution of this process assume their greatest simplicity when the substances to be separated differ so greatly in their volatility that, without appreciable error, one can be assumed to be non-volatile at the boiling point of the other. In the distillation of two substances of approximately equal molecular weight and latent heats of vaporization, supposing neither to predominate overwhelmingly over the other, the one with the lower boiling point will predominate in the early, and the other will gradually accumulate in the later, fractions of the distillate. And similarly with mixtures of three or more bodies. The further the respective boiling points are removed from one another, the more complete a separation can be effected; but in no case is the separation perfect. The effect of distillation can be increased by causing the vapour, before it reaches the condenser and to distil so slowly that a sufficiently large fraction of the vapour originally formed fails

to survive the ascent through the cooling influence of the atmosphere. The most effective method is to let the vapour ascend through a slanting condenser kept by means of a water bath at a certain temperature, which is controlled so that while the liquid in the flask boils rapidly, the distillation only first progresses and no more.

DRY DISTILLATION, ETC.

Besides distillation of the ordinary type, there are dry distillation, destructive distillation, fractional distillation.

Dry distillation is a term applied to the distillation of substances *per se*, or without the addition of water or any volatile liquid.

Destructive distillation is the distillation of substances at temperature sufficiently high to decompose them by which their elements are separated or evolved in new combination. This is adopted in obtaining tar from coal.

Fractional distillation is the separation of substances having different boiling points, by distilling the mixture at a gradually increasing temperature, and collecting the products which come over at different temperatures in separate receivers.

Condensation of the products in either straight line pipes or in coils may be brought about by air or water cooling. The materials of the still will require much consideration. It must resist the action of the chemical at the high temperature and be good conductor of heat and for still under vacuum where tight joints are necessary it must be capable of being machined.

FURNACE.

Furnaces suitable for chemical operations may broadly be classified under the following heads:—

- (a) Reverberatory Furnace.
- (b) Muffle Furnace.
- (c) Kiln Furnace.
- (d) Ordinary Furnace.

REVERBERATORY FURNACE.

The reverberatory furnace is only another name of open roaster (Fig. 2). The material to be heated is exposed to the direct action of the fire gases. The furnace consists essentially of an arched chamber built of brick and heated from a grate placed at one end while the products of combustion are removed by a chimney at the other end. The material is placed upon the bed of the furnace, the fire gases pass over it and are deflected by the arched form of the roof of the furnace so as to come more directly in contact with the charge. The inside of this furnace is lined with fire-bricks while the outside is built of common bricks.

When reduction of the substance is desired, the fire bars are placed close together and the fuel is charged to a thick layer while in case of oxidation the fire bars are set widely apart and fuel is fed in thin layers at a time.

MUFFLE FURNACE.

The muffle furnace differs materially from the reverberatory furnace. Here the fire gases are not allowed to come in contact with the substances to be calcined. The furnace consists of a muffle of fire brick but here the flues are so arranged that hot gases pass underneath the bed of the muffle and are then conducted over the top back to some point near the grate, where they are discharged into the chimney. A pipe is sometimes fitted to the top of the muffle, in order to discharge any gases which may be formed during calcination.

KILN FURNACE.

Kilns or shaft furnaces may be periodic or continuous and are mainly employed for the calcination of limestone. In periodic kilns the calcined charge is allowed to cool then withdrawn; and the kiln recharged with the same material. In the continuous form, the calcined material is drawn from the bottom at the same time that a fresh charge enters the top, the operation being a continuous one.

ORDINARY FURNACE.

In the case ordinary furnaces the fire place is made at the extremity of a narrow open space leading to the mouth of the furnace. Iron gratings are placed for proper airing. The ash pit is left just below the gratings. The mouth of the furnace may be provided with a suitable damper. On the side opposite the fire place there may be erected a chimney connected with the central opening for the escape of the smoke.

Either coal or fuel is fed into the fire place over the gratings and set fire to. The damper is adjusted for proper circulation of air and regulation of heat.

CHAPTER IV.

SULPHURIC ACID.

SULPHURIC acid is, without doubt, one of the most important of chemicals. For its varied uses in chemical technology it is regarded as the mother of all chemical industries. In fact, the statement is not an exaggerated one, because there is scarcely any industry in which this acid has not been employed in some form or other, and it has been asserted that the wealth of a country can be gauged by its production of sulphuric acid. This is certainly not strictly correct but sulphuric acid forms the starting point of so many major industries that there is a considerable element of truth in this statement. Nitric acid is prepared by a mixture of nitre and sulphuric acid while hydrochloric acid is produced by commercially treating common salt with chamber acid which is another name of sulphuric acid. The nitric and hydrochloric acids again in their turn are employed in manufacturing a wide range of chemicals used in various arts and industries.

USES.

At the present day, sulphuric acid is of special need in the following industries: (1) the manufacture of soil fertilisers which have an endless scope in an agricultural country like India; (2) for electroplating, storage cells and other requirements in the electrical sphere; (3) in the cotton and woollen mills for dyeing, for hide and leather; (4) in almost all the mining and metallurgical industries. There is besides, a very large number of

minor industries in which sulphuric acid constitutes an essential requisite.

DEMAND IN INDIA.

Probably about 77,000 tons of this acid is made annually at present in India. But one of the chief drawbacks to the expansion of the industry is the important raw material sulphur, which has to be imported from Japan, Sicily and other places. Pyrites which is often used in Continental works and contains 4 to 5 per cent. sulphur in admixture with sulphides of lead, zinc and copper occurs scattered about in various parts of India, and in one place, near Kaiabagh on the River Indus, it is sufficiently obtained in shales. Moreover, in this country may be found an almost unlimited supply of gypsum possessing from 16 to 20 per cent. of sulphur. It may be found possible to recover this sulphur for use in the manufacture of sulphuric acid. An analysis of consumption of sulphuric acid in India shows the following: Chemicals 21,000 tons, fertilisers 20,000 tons, metals 3,995 tons, cotton textiles 3,286 tons, mineral oils 1,611 tons, leather 790 tons, battery acid 410 tons, distillery 318 tons, etc. The demand is expected to rise to 150,000 tons in 5 years.

RAW MATERIALS.

The only raw materials required for this industry are sulphur and nitre. Instead of sulphur, any material, rich in sulphur, can be used with advantage. But as stated, India is not very favourably placed with respect to sulphur deposits. Minerals containing sulphur are abundant in many places of Madras Presidency, but owing to the high transport charges, the up-country manufacturers previously found it more economical to use Japanese

sulphur. An advantage of using Indian sulphur lies in the fact that it is practically free from arsenic, so that the acid produced with it is also arsenic free, which is a great advantage. The removal of arsenic from sulphuric acid is a very troublesome process and as there are a number of small industries requiring arsenic free acid, the Indian manufacturers are trying their utmost to capture these markets.*

Sulphuric acid may also be made from zinc blends which is available in Burma. There is every possibility of obtaining sulphur from it in near future as a bye-product. But it is problematic if this will be cheaper than iron pyrites.

OUTLINE OF THE PROCESS.

The outline of the process of manufacturing sulphuric acid on a commercial scale follows:—

The sulphur, in one of the forms in practice (viz. pyrites, spent oxide, or native sulphur), is burnt in a kiln by the heat of its own combustion, and the sulphur dioxide, mixed with air and with the nitrogen remaining in the air already used in effecting the combustion of the sulphur, meets with the nitric acid vapour, generated in nitre pots and immediately reacts with it, liberating oxides of nitrogen. This mixture of gases passes into leaden chambers where it meets with steam; a reaction producing dilute sulphuric acid occurs, in which all the constituents, save the nitrogen, are concerned. The latter gas has to be removed from the chambers by a draught. In order to avoid the carrying away of the oxides of nitrogen, which, although taking part in the reaction, are regenerated in the course of it, a column—the Gay-Lussac tower—down which strong sulphuric acid trickles, is interposed

between the chambers and the chimney. The oxides of nitrogen are absorbed by this sulphuric acid, and are re-introduced into the sphere of reaction in the leaden chambers by being expelled from the sulphuric acid by the heat of the gases from the pyrites kiln, which gases are caused to ascend a column—the Glover tower—placed between the pyrites kiln and the leaden chambers; the sulphuric acid, containing oxides of nitrogen, from the Gay-Lussac tower, is allowed to trickle down this column, the oxides of nitrogen being driven off and carried into the first chamber.

PROCESS AND PLANT.

For the production of the sulphuric acid some furnaces are necessary for burning the pyrites, sulphur, or other sulphur-containing material. The construction of these differs somewhat with the nature of the substance to be burnt. The description of pyrites burners, sulphur burners and nitre pots follows:—

PYRITES BURNERS.

Pyrites Burners are of two forms:—(1) Burners for lump pyrites, and (2) burners for “smalls,” i.e., powdered material. Burners for lump pyrites consist of fire-brick chambers, about 6 ft. \times 5 ft. \times 4 ft. with slightly sloping sides, set in pairs and provided with grate made of iron bars of square section which can be rotated at will. The pyrites rests on this grate and as it burns the iron bars are rotated, allowing the burnt ore to drop out. The burners are fitted with two doors, one at the top for charging the pyrites, and a smaller one lower down for adjusting the burning charge. In burning, not only has enough air to be introduced to oxidise both sulphur and iron of the

pyrites but also sufficient to convert the whole of sulphur dioxide formed into sulphuric acid by the acid of the nitrous gases that act as carriers of oxygen. In the actual management of the burners, the two main objects to be attained are the conversion of the maximum amount of the sulphur content into sulphur dioxide and the avoidance of the formation of clinker ("scars") due to the fact that defect of air allows of the production of the fusible sulphide. As the complete combustion of the sulphur of the pyrites cannot be effected without an excess of air more than sufficient to serve for the subsequent oxidation of sulphur dioxide to sulphuric acid, the efforts of the manufacturer are directed to the keeping of the air supply as small as is consistent with the above conditions.

Not only do the smaller fragments of crushed pyrites need to be burnt in furnaces different from those used for lump pyrites but spent purifier from gas works has also to be treated in a similar manner. The burner for smalls must be so arranged that the material is spread in a fairly thin layer, inasmuch as the kiln form, described above, would be speedily choked. The smalls burner consists of a rectangular firebricks box provided with horizontal fire clay shelves, so arranged that the smalls can be raked from one to the next below by a rake inserted through the opening. The smalls are fed through a hopper and when they have been distributed on the shelves, the combustion is started by the fire on the grate. The smalls, when once ignited, evolve sufficient heat to maintain the combustion. When the burner is working normally the whole of the necessary air is admitted through the lowest door, and the smalls are only completely burnt on reaching the lowest shelf. Various mechanical burners for crushed

pyrites (smalls) have been devised, the object in view being to keep the pyrites stirred, and thus constantly expose fresh surfaces to oxidation.

SULPHUR BURNER.

When acid is made from sulphur, the simplest form of burner consists of an iron tray, on which sulphur is thrown from time to time, and there volatilised and burnt. In better forms of burner, provision has to be made for the complete combustion of such sulphur as is sublimed. This is effected by the addition of fire brick towers into which a subsidiary supply of air is introduced to cause complete combustion. When sulphur is used as raw material, the air is required to oxidise, sulphur only and not iron, whence it results that the exit gases are richer in sulphur-dioxide and poorer in nitrogen than those from pyrites burners.

NITRE POTS.

The sulphur dioxide obtained by any of the above methods is led by a flue, common to a set of burners, to the Glover tower. In this flue one or more nitre pots are set. These consist of cast-iron vessel placed in the flue beneath hoppers by which the nitre is charged in quantities, sulphuric acid being introduced into it through a syphon to decompose the nitrate and liberate the nitric acid. The pots are fitted with a waste pipe, running through the wall of the flue, whereby the liquid nitre-cake can be withdrawn when the charge is exhausted. Much dust is liable to be deposited in the flue, particularly when crushed are burnt. Where this deposit is large, it is needful to lead the flue into a dust chamber before it enters the Glover tower. This chamber is an enlargement of the

flue, provided with baffle plates, in which the rate of the current of gases is diminished and the stream mechanically broken up throws down the dust.

GLOVER TOWER.

The Glover Tower is a strong structure with leaden walls lined with refractory and acid-proof fire-brick, and filled with some acid and heat-resisting material, such as flint or fire-brick, arranged so as to distribute evenly liquid trickling down the tower. It is supported on brick arches. Underneath which the pyrites flue enters the tower. The upper part of the tower, where the temperature is lower, may consist of a plate column. At the top of the Glover tower is a tank containing the chamber acid and the nitrous vitriol from the Gay-Lusac tower; this tank supplies a distributing arrangement worked by the reaction of the acid flowing from its radial arms. The exit pipe for the gases which ascend the tower is at the top, and is connected with the first chamber, as shown in Plate I.

VITRIOL CHAMBERS.

Vitriol Chambers are invariably made of lead and consist of rectangular "curtains" standing in "saucers," which are large, flat trays, the edges of which are turned up to a height of 12 to 15 inches. The sheets of lead composing the curtain, and those of which the saucers are made, are autogenously soldered and are fastened to the framework of wood which supports them by lead straps attached to the wood by nails coated with lead. The whole arrangement resembles a box with a loosely-fitting lid turned upside down. The whole is gas-tight, on account of the saucer containing enough acid to seal the edges of the curtain. The number of chambers and their

size vary in different works. Usually, from two to four is used, and the size varies from 100 to 130 ft. \times 25 to 30 ft. \times 16 to 20 ft. in height. The chambers are connected by lead tunnels, and the last of the series communicates with the bottom of the Gay-Lussac tower, described below.

GAY-LUSSAC TOWER.

The Gay-Lussac Tower is arranged like the Glover tower, and is of similar dimensions. A cistern at the top contains acid of sp. gr. 1.75 which is pumped into this position from the "acid egg." The acid flows from the cistern into a distributor similar to that used for the Glover tower.

In view of the fact that the acid which has passed down the Gay-Lussac tower has to be raised to the top of the Glover tower, for efficiency of work it is customary to build the towers side by side.

LUNGE-ROHRMANN PLATE COLUMNS.

Instead of relying on mere chamber space for the mixing and reaction of the gases, smaller chambers are now often used, with interposed plate columns, through which the gases must pass in going from one chamber to the next, whereby an economy of chamber space is possible. These columns consist of a lead-lined tower fitted with horizontal stoneware-plates, which are perforated, each perforation having raised edges and being surrounded by ridges, so that there may be always a little pool of liquid ready to overflow and drop through the perforation on to the next bottom plate, which is so constructed that the drop may fall on the surface of the plate but does not fall through a hole.

By this process much liquid condenses in this column which will assist much in the formation of sulphuric acid. These Lunge-Rohrmann plate columns, as they are termed, are often used in conjunction with ordinary Glover and Gay-Lussac towers.

CONVERSION OF SULPHUR DIOXIDE INTO SULPHURIC ACID.

The sulphur dioxide prepared in the pyrites burners passes into the Glover tower accompanied by nitric acid vapour from the nitre pots, and sufficient oxygen (derived from the excess of air necessary to burn the pyrites). As soon as this mixture of gases reach the chambers from the tower, they come in contact with steam, which is injected by the jets supplied from a boiler, forming sulphuric acid. The most probable explanation of its formation from these gases, and of the way in which the oxide of nitrogen serves as a carrier of atmospheric oxygen to sulphur dioxide is that the mixture on coming in contact with steam first forms nitrosyl-sulphuric acid, which at once re-acted with further amount of steam splits up into sulphuric acid and oxide of nitrogen, the cycle of changes being then repeated.

The sulphuric acid generated in the form of mist gradually rains down upon the bottom of the chamber. On account of the need for thorough intermixture of the reacting gases and of the condensing influence of a considerable surface upon them and upon the mist of sulphuric acid formed, it is found inexpedient to use one large chamber, two or more of moderate size being preferable, and, recently, small lead chambers, or even plate columns between large chambers, as referred to above, have been tried with satisfactory results.

The unabsorbed gases from the last chamber is allowed to pass up the Gay-Lussac tower where they encounter with the vitriol flowing downwards. The oxide of nitrogen is thereby absorbed and transferred to the top of Glover tower so as to react with fresh burner gases.

The acid which collects on the floor of the chambers is generally known as Chamber acid and is continually tested during the working of the process to ascertain its specific gravity, which in any case may not exceed 1.625. Otherwise, it is likely to corrode the lead. The condensed acid is finally taken out of the chamber from time to time.

REGULATION OF THE PROCESSES IN THE LEAD CHAMBERS.

Since pyrites are generally used in the manufacture of Chamber acids, it is necessary to regulate the draught so that the furnace gases contain about $7\frac{1}{2}$ per cent. by volume of sulphur dioxide and the final gases which escape from the chamber from $6\frac{1}{2}$ to $7\frac{1}{2}$ per cent. by volume of oxygen.

The entry of the steam is regulated in such a way that the acid formed in the chamber is maintained at a definite concentration of 50° to 53° Be, but that in the last chamber, into which no steam is injected, and in which the gases are poor and partially exhausted, is sometimes only at 40° Be. The acid which falls from the roof and the walls varies rather rapidly in concentration with the variation in the amount of steam and is ordinarily more concentrated by 2° to 3° Be, so that an excess or deficiency of steam may be detected by frequent titration of the acid, which is collected through suitable apertures and channels constructed along the internal walls of the chamber.

The temperature inside the lead chamber rises or falls with increase or diminution of nitrate, and if the temperature of the vapours which enter the chamber is 70° to 90°C then the most suitable mean temperature in the first chamber is about 65°C ., whilst in the second chamber it is 55°C ., and in the third about 35°C ., although in some works temperatures of about 100°C in the first chamber are advantageously employed. The lead is then more rapidly attacked, especially if the quantity of nitrous fumes is not very carefully regulated. The gases are led from the last chamber through a leaden tube to the base of the Gay-Lussac tower. The colour of the vapours in the first chamber should be very pale and should gradually change as one gets further from the point of entry, requiring a more and more interest yellowish-brown colour, and at the entrance to the Gay-Lussac tower should be markedly reddish-brown. The gases which escape from this tower should be colourless.

The acid which collects at the base of the chamber is removed from time to time, but to an extent of not more than 10 c.m. each time, a layer of at least 20 to 30 c.m. being always left.

The most important control of the process of the reactions in the lead chambers is effected by watching the work of the towers, which for convenience should be placed close together, and by analysing the escaping gases by the usual analytical methods. The sulphur dioxide of the furnace gases is titrated with a deci-normal solution of iodine by Reich's method.

CONCENTRATION.

The acid which is collected in the chambers contains 0—70 per cent. acid which is concentrated in the Glover

tower to about 78 per cent. But the Glover acid is contaminated with considerable quantity of arsenic oxide, ferric oxide, etc. which are very difficult to remove. To avoid these, the acid is generally concentrated by evaporation in lead or porcelain pans by the waste heat of the furnace. Recently however pans of extremely acid-resisting materials have been placed on the market.

The pans, usually 20 in number, are arranged in a series of steps with the chamber acid in the highest pan. The acid flows from pan to pan as it is concentrated up to 98 per cent. A considerable quantity of acid fumes is evolved, so that the basins are covered with a hood which carries the fumes to a condensing system. Sulphuric acid can be concentrated by evaporation up to 98 per cent, boiling at 338°C . The ordinary commercial acid contains 93.5 per cent. acid.

PURIFICATION.

Chamber acid contains oxides of Nitrogen, lead sulphate, and arsenic. During its passage down the Glover tower it takes up iron. The most objectionable of these impurities is the arsenic, which passes into the hydrochloric acid produced in the manufacture of salt cake. Arsenic is eliminated by passing sulphuretted hydrogen gas through the chamber acid and allowing the precipitated arsenic to settle. Arsenic free vitriol is, however, best made from native sulphur which does not contain arsenic. In this connection the Indian manufacturers gained the advantage because they are extensively using it owing to the scarcity of pyrites in this country. Oxides of nitrogen are got rid of by heating the acid with ammonium sulphate before it goes into the platinum stills, where this impurity would cause corrosion. Iron and lead are

allowed to remain in commercial acid. When almost pure acid is required, the comparatively weak distillate from the platinum stills is concentrated and utilised. Instead of treating the chamber acid in this elaborate way, which merely increases the cost of production, it is better to use native sulphur in place of pyrites.

SULPHURIC ACID BY THE CONTACT PROCESS.

From the foregoing account of the chamber process, it will be understood that the oxidant used—the higher oxides of nitrogen—presents certain disadvantages. It necessitates a large reaction chamber, is easily removed from the sphere of action, and cannot be profitably used unless a comparatively dilute acid is produced. The first and second of these disadvantages, and in a measure the third also, are due to the gaseous, character of the oxides.

It has been known for nearly a century that certain solid bodies, notably finely divided platinum, will induce the direct combination of sulphur dioxide and oxygen to sulphur trioxide, without suffering any appreciable chemical change themselves as a result of the combination. Pure sulphur trioxide free from arsenic, etc., when dissolved in water, gives sulphuric acid, which may be even fuming at a high concentration.

The sulphur dioxide used in the contact process is obtained by roasting lump pyrites as in the case of chamber acid. The burners consist of fire brick chambers with slightly sloping sides, set in pairs and provided with a grate made of iron bars. The pyrites rests on this grate to a depth of 2 to 3 feet, and as it burns the iron bars are rotated allowing the burnt ore to drop out. The burners are fitted with two doors, one at the top for charging the pyrites and a smaller one lower down for adjusting the

burning charge. In burning, enough air should be introduced to oxidise sulphur in the pyrites. The gases when leaving the pyrites burner, must contain enough oxygen for their subsequent oxidation to sulphur trioxide.

The gases must be very carefully purified before entering the contact chamber as arsenic, and to a smaller extent antimony and mercury are especially fatal to the activity of the contact mass. After leaving the roasting kiln whilst still very hot the gases are thoroughly mixed by blowing in a jet of steam. This serves two purposes: the last traces of sulphur always present, which carry arsenic, are burnt to sulphur dioxide and the sulphuric acid obtained during the subsequent cooling of the gases from the small amount of sulphur trioxide present in the kiln gases, is so diluted that it does not attack the condensing apparatus. This consists mainly of long pipes in which the gases are slowly cooled; the parts with which the condensed sulphuric acid comes in contact must not be made of iron but one of the worst "contact poisons," arsenuretted hydrogen, be evolved by the hydrogen formed. Rapid cooling of the gases is inadmissible, for many of the impurities may thus escape condensation. After leaving the condensing apparatus, the gases are thoroughly washed with water or dilute sulphuric acid either by being forced through wash bottles containing the liquid, or else by mechanically agitating the liquid in pipes which the gases are made to traverse.

The pure gases, consisting of sulphur dioxide, oxygen, and nitrogen, then reach the contact chamber. It is to be noted that the temperature inside this, if left to itself after the reaction was once started, would soon far exceed that required for economical working. The temperature at which the desired reaction proceeds most smoothly ap-





appears to lie between 300° and 400°C and when this rises to about 450°C reversible reaction takes place. Some system of cooling the chamber is therefore necessary, one of the two following methods being used:—

According to the first system, the entering gases may be used to cool the chamber from the outside, entering it finally at the lowest temperature at which the reaction proceeds. The cold gases enter the outer space surrounding the pipes containing the contact mass, either by first passing through a chamber in which their temperature may be adjusted into the gas chambers from which they are evenly distributed or by directly entering the pipe through a valve. This pipe is also leading to control pipes which traverse the whole outside space, and have small openings through which the gases emerge into outer space surrounding the pipes. The space between the contact pipes is partly blocked by a number of partitions which force the gases to pass close to the walls of the pipes. From the outer space surrounding the contact pipes, the gases enter the mixing chamber, where their temperature is equalised, and then pass through the pipes containing the contact mass, emerging finally into the exit pipe. A cooling chamber is occasionally introduced between the outer space surrounding the contact pipes and the mixing chamber. The whole chamber is heated at the commencement of the reaction by flue gases. This heating is, of course, discontinued as soon as the reaction has started. (Fig. 4.)

The contact mass itself generally consists of platinised asbestos or pumice, prepared by dipping the latter substances into solutions containing a platinum salt and some organic reducing agent, such as sugar, drying and igniting the mass at a red heat. Occasionally a contact

substance is used which has been obtained by evaporating a solution containing an alkali sulphate or phosphate and a platinum salt to dryness and igniting the residue. It has the advantage that the platinum may easily be recovered from it after it has become inert, by simple dissolving out the alkali salt with water. Substances such as ferric oxide have also been proposed as contact substances, but their use has been attended with little success.

After leaving the contact chamber, the gases should consist only of sulphur trioxide and sulphuric acid vapour, nitrogen and a little oxygen. The sulphur trioxide is absorbed by sulphuric acid containing 97 to 98 per cent. H_2SO_4 , acid of this strength being capable of removing sulphur trioxide, almost instantaneously, even from a rapid current of gas, whilst water or weaker sulphuric acid are far less effective absorbents. The absorbing apparatus is made of wrought iron, which is scarcely attacked provided the strength of the acid is not allowed to fall below 27 per cent. free sulphur trioxide. The final product of the process thus consists of fuming sulphuric acid; by drying the gases with strong sulphuric acid before they enter the contact chamber, and condensing the exit gases by means of external cooling only, sulphuric anhydride (SO_3) may also be obtained. Very strong sulphuric acid may also be readily obtained by diluting the fuming acid with the calculated amount of water or weaker sulphuric acid, thus saving the costly concentration necessary when such acid is made from chamber acid.

THE BADISCHE PROCESS.

Details of the Badische Process follow. In this sulphur dioxide is washed with sulphuric acid and passed

through coke filters, heat exchangers, convert using plan-
nised asbestos and absorbed in strong sulphuric acid.

The method of producing the sulphur dioxide is the same as that described in the chamber process and need not be repeated here.

CATALYSTS.

It has been found that a very small amount of arsenic in the gas greatly reduces or "poisons" the activity of platinum catalysts. The volatile compounds of selenium, antimony, lead and some other metals have a similar "poisonous" effect though less severe. Chlorine, hydrogen chloride and hydrogen fluoride temporarily retard the activity of the catalyst. Even dust particles reduce the power of conversion of the catalytic mass. Hence the gas must be scrupulously pure and free from the above impurities for a successful working of the process.

The catalyst employed in the Badische process is platinumised asbestos and is prepared by first washing the long fibred Italian asbestos in hydrochloric acid and nitric acid respectively. The washed fibres are then soaked with a 10% solution of platinic chloride containing a reducing agent such as glucose or sodium formate and heated. The asbestos may be woven in the form of rope mats (Mannheim process) or fluted into a loose mass (Badische process). It usually carries 6-10% of its weight of platinum and if the gases be properly purified, the life of the catalyst ranges from 10 to 15 years.

The hot burner gas admixed with steam is slowly cooled in a dry cooler consisting of cast pipes exposed to the atmosphere. The temperature is not allowed to fall below 275°C otherwise the traces of sulphur trioxide that are always present may react with steam and condense as

sulphuric acid drops corroding the iron pipes. The gas then passes through a "Cottrol Dust Separator" which separates the dust particles electrostatically.

The gas then passes through one or more scrubbing towers made of acid proof construction lined with brick and filled with a loose packing of quartz down which trickles sulphuric acid of 92-98% strength. The amount of acid is regulated so as not to over dry the gas.

It is then passed through a bed of coke filters under a pressure of 5" to 8" of mercury by means of a blower. The first layer of the bed consists of 4" lumps upon which is a 6" layer of sizes graduated to $\frac{1}{4}$ ". This is followed by a layer of finer particles, grading down in the size to about 1 mm, extending to a depth of several feet. The area usually provided is 1 sq. foot for every 85 cubic feet of gas per hour. When it becomes necessary to renew any filter, as indicated by the stoppage of the draft, only the top layers are removed and replaced with equal amount of fresh coke of the same size. If the filters are working properly, a concentrated pencil of light of the intensity of direct sunlight is entirely invisible when thrown through the gas and this test is applied before the gas is allowed to enter the contact mass.

PRE-HEATING THE DIOXIDE.

During the step II the gas gets considerably cooled and so its temperature is to be raised to the proper "ignition point" to effect the conversion. This is done by a couple of pre-heaters or heat exchangers which are vertical steel cylinders closed at both ends having an inlet and an outlet at the top and bottom for the sulphur trioxide from the converters. There is also another pair of inlet and outlet at the sides for the un-converted gas between a pair of

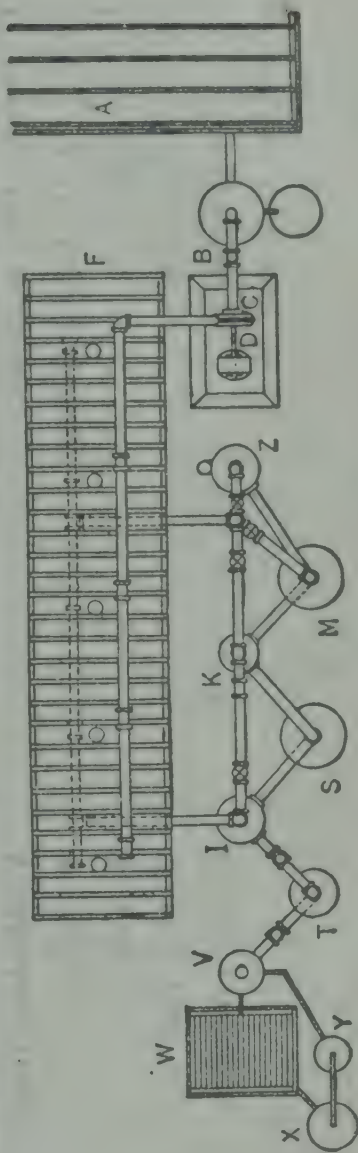
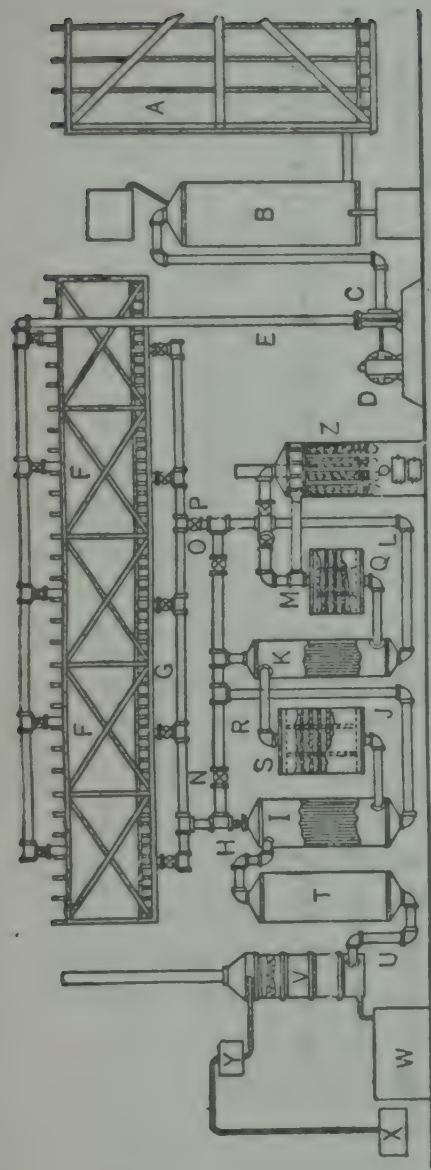


FIG 5. BADISCHE PROCESS.

[Page 55.

For particulars see reverse.]

A—Cooling & Dust Separating Apparatus.

B—Scrubbing Towers.

C—Blower.

D—Motor to Drive the Blower.

E, G, J, Q, U,—Conducting Pipes.

F—Coke Filters.

H, N, O, P,—Valves.

I—1st Heat Exchanger.

K—2nd Heat Exchanger.

M—1st Converter.

S—2nd Converter.

T—Tubular Air Cooler.

V—Absorbing Tower.

W—Cooler.

X—Tank.

Y—Feed Tank.

Z—Coal Fired Heater.

parallel steel discs having perforations connected by tubes of $1\frac{1}{4}$ - $2\frac{3}{4}$ " in diameter and 10-15" in length. The number of tubes vary from 100 to 600 according to the capacity of the heat-exchanger. (Fig. 5.)

During the working of the process, the dried and purified gas from step II enters the 1st heat-exchanger at the side and passes upward surrounding these tubes, and is led to the second exchanger in the same way. Then it enters the first converter where the greater portion of the conversion takes place and the temperature is raised due to the exothermic nature of the reaction. The hot and partially converted gas then enters the 2nd exchanger from above and passes down the narrow tubes to the 2nd converter, heating the in-coming sulphur dioxide surrounding them. On its exit at the bottom from the 2nd exchanger, the partially converted gas is led to the 2nd converter for complete oxidation. The hot and fully converted gas enters the 1st exchanger in the same manner before it is led to the cooler prior to absorption in the same manner before it is led to the cooler prior to absorption in the strong acid.

The pre-heated gas (mainly 8 % sulphur dioxide admixed with double the amount of oxygen theoretically necessary, in the form of air) enters the 1st converter from the top at a temperature of 400° - 405°C and is forced down the contact material whereby about 85% of the conversion takes place. The hot and partially converted gas is led to the 2nd converter through the 2nd heat-exchanger as explained above at about 405°C where the conversion is completed (about 98% conversion).

Each converter consists essentially of a vertical cylindrical shell divided into a number of superposed chambers by perforated cast iron shelves each containing

a layer of platinised asbestos. The 2nd converter is usually larger and carries a richer and greater amount of platinised asbestos than the 1st converter. There are usually 50 shelves spaced 1" apart each containing a layer of platinised asbestos $\frac{1}{2}$ " to $\frac{3}{4}$ " thick or even more if the shelves are fewer in number. Coal fired heater is used when starting the plant but as the reaction develops, the heat evolved during the process is sufficient to maintain the temperature, and external heating becomes unnecessary. Very careful regulation of the temperature is to be maintained of the entrance and various other points in the 1st converter for a successful working of the plant.

COOLING THE DIOXIDE BEFORE ABSORPTION.

During the passage of the gas through the 1st heat-exchanger from the end converter, it is considerably cooled by giving away its heat to the cool incoming sulphur dioxide. The temperature is further lowered to 150°C in tubular air coolers for efficient absorption of sulphur trioxide in strong sulphuric acid.

ABSORPING THE TRIOXIDE.

The sulphur trioxide enters the absorption tower at the bottom and during its upward passage is absorbed by strong sulphuric and of 98.5% strength flowing down the tower through a bed of loosely packed quartz or porcelain. The construction of the tower is similar to that of Glover tower described in the chamber process. Sulphur trioxide is very difficult to be absorbed in water on even in weak acid and hence strong (90%-99%) acid is used to absorb the trioxide. The brown, oily, fuming liquid, called fuming sulphuric acid, is withdrawn at the bottom of the tower and is diluted with water to any desired strength.

phuric acid produced by this method is water white in colour and very pure. It is only with expensive and tedious distillation that the acid made by the chamber process may be made comparable to that made by the contact process.

SULPHURIC ACID FROM GYPSUM.

For some years attempts have been made to utilise sulphur present in gypsum for the manufacture of sulphuric acid. Since 1905 patents have been filed for various processes in which the sulphuric acid or sulphur dioxide of the sulphate is liberated at a very high temperature in presence of silica, carbon, etc.

STORING AND HANDLING OF SULPHURIC ACID.

Chamber or tower acid is usually stored and conveyed in lead-lined wooden tanks. Vessels are now made of acid-resisting steel, glass-enamel coated steel, and homogeneous lead-coated iron. All of these have their advantages, however.

For acid of 140° Tw. or over, steel or iron vessels may be safely employed if a few precautions are observed. The vessel must not be closed to the outside air, as hydrochloric acid might be evolved therein, and considerable pressure built up, and the vessel should not be left entirely empty, as moisture is likely to be absorbed, and severe corrosion takes place near the air-acid surface. In order to avoid a compromise, the wisest plan is to employ a vent-pipe sealed in a few inches of strong acid, and so arranged that air can be drawn in or driven out through it.

In smaller quantity bottles or glass carboys are used of all strengths.

CHAPTER V. IRON SULPHATE.

FERROUS sulphate or green vitriol occurs abundantly in nature in the form of green crystals. The natural sulphate, known as green copperas, is formed by the weathering of iron pyrites. It is found in various parts of India. It is commonly known as *hirakash*. It is generally obtained from the decomposition of pyrites or marcasite. Iron sulphate is also frequently found in solution in the drainage water from mines, and from this source it is manufactured on a large scale.

PROCESS OF MANUFACTURE.

1. Moistened iron pyrites are piled up in heaps and exposed to the air for several months. By the influence of the atmosphere it is converted into iron sulphate and some free sulphuric acid.

The soluble ferrous sulphate together with the free sulphuric acid is run into an underground tank where the excess of the acid is removed by the action of scrap iron. The solution is then evaporated on large pans and the large crystals of ferrous sulphate are obtained.

2. Ferrous sulphate is also formed as a bye-product in the manufacture of copper sulphate or blue vitriol. After the separation of the copper sulphate crystals, the mother liquor contains iron sulphate and some copper sulphate. From the liquor the copper is precipitated by scrap iron and iron sulphate remains in the solution which is then evaporated to crystallisation. But still it contains

aces of copper sulphate and ferric sulphate, together with the sulphate of zinc, manganese and other metals. By recrystallisation, copper and ferric sulphates can be removed but sulphate of zinc, manganese and other salts cannot be got rid of.

3. Ferrous sulphate can also be prepared by dissolving sulphide of iron in water. Iron and sulphur are calcined in a potter's furnace until it becomes red. Upon this distilled water is poured and a fine green liquid is formed. This liquid is drawn off and evaporated to crystallisation.

MEDICINAL PREPARATION.

Chemically pure ferrous sulphate is best prepared by heating an excess of iron wire with dilute sulphuric acid. When the evolution of hydrogen has ceased, the liquid is boiled together with the undissolved portion of the wire. The solution is then filtered and evaporated to crystallisation. The process follows:—

Iron wire, 4 parts; sulphuric acid, 4 parts; distilled water, 30 parts. After putting the wire in a stoneware or porcelain vessel the water is poured over it and then the acid is also added. When the disengagement of gas has nearly ceased, the whole is boiled, for 10 minutes and filtered. The liquid is then allowed to settle for 24 hours when the crystals of ferrous sulphate collect at the bottom of the vessel.

This impure sulphate of iron is then taken out and for every 4 lbs. of its weight, 1 oz. of sulphuric acid, and 2 pints of water are added. 1 oz. of iron wire is also added to the mixture to remove the residual sulphuric acid. The mixture is then heated with occasional agitation until the sulphate is dissolved. The solution is strained whilst hot and set aside to crystallise.

To obtain more crystals the mother liquor left after the separation of ferrous sulphate is further concentrated and set aside as before. The crystals are separated from the liquor and kept in well stoppered bottles.

PROPERTIES.

Ferrous sulphate forms pale green, mono-symmetric crystals which effloresce on exposure to the air. Its specific gravity is 1.89 at a temperature of 4°C .

It is insoluble in concentrated sulphuric acid and absolute alcohol but very slightly soluble in dilute alcohol.

It crystallises with seven molecules of water and forms an anhydrous salt. Hydrates with two or three molecules of water are also known. When septa hydrate is left exposed to the air, it gradually loses its water and is converted into basic ferric sulphate. In European medicines it is used as an astringent and stimulant for local application.

Ferrous sulphate is largely used in arts and manufactures for the preparation of iron mordants, inks, prussian blue, etc. For dyeing purpose, it is generally mixed with organic substances to obtain various colours such as grey, black, green, brown, purple, etc. It is much used in calico printing. In certain places of India the natural copperas is employed for these purposes and in others such as Lucknow it is prepared artificially by placing bars of iron in a vat containing a solution of coarse sugar, etc. The weight of iron used is about four times the sugar dissolved. When the solution has become of a deep red colour, it is ready for dyeing purpose. Myrobalans are occasionally added to clear the colour.

CHAPTER VI.

SULPHATE OF COPPER.

COPPER sulphate, blue stone or blue vitriol, is one of the most important salts of copper. The ancient Hindu chemists prepared it by roasting the pyrites, dissolving the roasted ore in water and evaporating the solution to crystallisation. In the West, it was first prepared by Simon Helmout in 1644. He prepared it by roasting together the copper and sulphur, and then moistening the mass with rain water. After four years, that is, in the year 1648, Glauber experimentally showed that this salt could be prepared by heating copper with sulphuric acid.

The following are the principal ores from which copper sulphate may be prepared:—Copper pyrites, argentiferous copper ores, malachite, olivenite, etc.

The chief methods of manufacturing copper sulphate both on a small and big scale are given below. The process of manufacture is not at all difficult and no costly machinery is required for the purpose.

COPPER SULPHATE FROM COPPER PYRITES.

Copper sulphate is principally obtained from copper pyrites. The ore is carefully roasted whereby it is oxidised to copper sulphate, and the iron which is present in the ore is also oxidised to ferrous and ferric oxide. The roasted mass is then lixiviated and the copper sulphate goes into solution. The clear solution is then decanted and evaporated to such concentration that will deposit crystals on cooling.

The whole of the sulphate cannot be recovered in this process, for the mother liquor contains a double sulphate of copper and iron, which cannot be entirely separated by crystallisation. From this liquor copper is separated by precipitating with scrap iron. The precipitated copper is then treated separately for the manufacture of the sulphate. For manure and other agricultural purposes, the presence of iron sulphate is not injurious. Therefore, for those purposes, the mother liquor can be directly concentrated.

COPPER SULPHATE FROM ARGENTIFEROUS COPPER.

Argentiferous copper ore is roasted in the hearth or a reverberatory furnace. The roasted ore is then treated with a small quantity of dilute sulphuric acid till the solution is distinctly acid. Lead, gold, etc. which may be present in the ore are left undissolved. The solution which contains silver, arsenic, copper, etc. is then decanted and poured into wooden tanks lined with lead. Strips of copper are introduced into the solution. Silver and portions of arsenic and antimony, if present, are deposited. If bismuth be present, it is separated as basic sulphate. Thus almost a pure copper sulphate solution is obtained. The solution is then evaporated in large lead-lined tanks and the crystals are formed on strips of lead hung in the solution for the purpose.

COPPER SULPHATE FROM SULPHIDES.

Copper sulphate is obtained as a secondary product in a silver refinery process. The ores containing sulphides of silver, copper and iron are roasted. At first the sulphides are converted into sulphates. As the roasting continues, the sulphates are gradually converted into

oxide. When the whole of iron sulphate is oxidised and the copper sulphate begins to oxidise, the process is stopped. The roasted mass is then lixiviated with water; the silver sulphate and the remaining portion of copper sulphate go into solution. Scrap copper is then introduced into the solution. The silver is precipitated leaving behind the copper sulphate solution. From this solution the crystals are obtained in the usual way.

COPPER SULPHATE FROM METALLIC COPPER.

Copper sulphate is also obtained by directly dissolving the metal in concentrated sulphuric acid; for this purpose copper and sulphuric acid are heated together. The metal is oxidised by a portion of the oxygen of the acid, while sulphurous acid escapes. The crude copper obtained by smelting the ore, and containing about 60 per cent. of metal is treated with sulphuric acid. The resulting solution is evaporated in leaden vessels and the clear liquid is left to crystallise in copper pans. From the mother liquor of the crystals, metallic copper is precipitated by means of iron, because the presence of a large quantity of iron sulphate renders this mother liquor unfit for further making of the vitriol. This method of obtaining copper sulphate is the least expensive but the salt is not quite pure.

II.

If the copper scraps, turnings, borings, etc. are previously converted into copper oxide by exposure to a red heat, only half the quantity of sulphuric acid needed when the metal and the acid are heated directly, is required. On a large scale it is manufactured as follows:

Sheets or scraps of copper are heated to redness in a reverberatory furnace to the boiling point of sulphur. A

quantity of sulphur is thrown in. The furnace door and other openings are closed tightly, the effect being the formation of copper sulphide. After some time air is admitted into the furnace whereby the sulphide is converted by a comparatively low heat and the action of the oxygen into sulphate. The mass is next placed in a suitable vessel and as much sulphuric acid is added to it as is sufficient to saturate the oxide of copper. The clear solution, having been decanted from the insoluble residue is set aside for crystallisation.

Copper sulphide ores, etc., and the acid dipping liquors from copper and brass works are also used for the preparation of copper sulphate. But the salts obtained from them are very impure, as a great number of foreign metals are associated with them.

The sulphate of copper contains a small quantity of iron which can be removed by either of the two processes mentioned below—

(a) By roasting the salt until the iron sulphate is converted into oxide, and then lixiviating the mass and recrystallising.

(b) By boiling the solution with a little nitric acid or lead peroxide until the sulphate of iron which is present in the ferrous condition is converted into ferric state. This ferric sulphate being very soluble remains in the solution on crystallisation.

Copper sulphate may be further purified to perfection by dissolving in distilled water and then evaporating to crystallisation.

PROPERTIES.

Copper sulphate forms large blue asymmetric crystals with five molecules' of water. Its specific gravity is 2.28. It is slightly soluble in dilute spirits but insoluble in abso-

ate alcohol. When heated to 100°C for some time it loses four molecules of water and a bluish white powder is left behind, which when heated to about 220°C loses the residual molecule of water and an anhydrous white powder is left behind. This anhydrous salt is extremely hygroscopic and readily absorbs water and becomes blue.

Copper sulphate is largely used in calico printing principally in connection with potassium dichromate or iron mordant. It is also required in the preparation of copper pigments such as lime blue, copper chromate, blue verditer; in making copper logwood inks; in black-dyeing with logwood; to prevent rot in timber and for making it fire-proof. It is also used in making germicides and insecticides and in inverting sucrose (cane sugar and beet sugar) into glucose and fructose. Copper sulphate is also used in a very large quantity in the electro-metalurgical processes and as an analytical reagent. It is also used in dyeing to make diazo colours permanent to light. The dyed fabrics may be treated with the salt or it may be added in the diazotising bath.

Blue vitriol serves for the manufacture of copper acetate, for bronzing iron, for bringing out the colour of alloys of gold. It is also used for galvanoplastic purposes.

CHAPTER VIII.

EPSOM SALT.

EPSOM Salt is a hydrated form of magnesium sulphate. It is used for sizing cotton fabric and in pharmacy. Magnesium sulphate is found native in British Columbia. In Germany it is one of the numerous salts prepared from the well-known potash deposits at Stassfurt and most of the magnesium sulphate imported into India is generally obtained from that source. Large quantities are also made artificially, usually by dissolving magnesite (natural magnesium carbonate) in sulphuric acid and crystallising the solution so obtained. Epsom salt is now-a-days manufactured in India from the mother liquor or bitterns obtained after the separation of common salt (sodium chloride) from sea water.

METHOD OF PREPARATION.

The method usually adopted is as follows. Bitterns from the salt pans are collected and further evaporated by the heat of the sun. At this stage the residual common salt present in the bitterns is crystallised out and at the same time other salts are also thrown down. The liquor, now rich in magnesium chloride, is then heated in copper pans and concentrated to such an extent that the boiling point becomes 135°C . By this means magnesium sulphate, which has up till now existed as epsom salt ($\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$), loses water of crystallisation and is converted into another sulphate known as kieserite

$\text{MgSO}_4 \cdot \text{H}_2\text{O}$). This kieserite is practically insoluble in a saturated solution of magnesium chloride and hence thrown out of solution. The liquor is then pumped into a settling tank, where the whole of kieserite falls to the bottom and is separated out from the liquor which now only contains magnesium chloride, which can be recovered by crystallisation.

PURIFICATION OF KIESERITE.

The kieserite obtained in this way contains a small amount of chloride. It is very difficult to separate the salt from each other. Although kieserite is practically insoluble in saturated solution of magnesium chloride, it is fairly soluble in a weak solution; hence it is not advisable to separate it out by fractional crystallisation.

It has been found, however, that on treatment with sulphuric acid, quantitative decomposition takes place, the whole of chloride being converted into sulphate with the evolution of hydrochloric acid. The sulphate can be removed from the still, which is of course acid-proof and practically pure magnesium sulphate or epsom salt can be obtained on crystallisation.

CHAPTER VIII.

GLAUBER'S SALT.

SMALL quantities of sodium sulphate which otherwise known as Glauber's salt are found in the sea water. Preparation of Glauber's salt from this source on an industrial scale is only possible, when the liquid has been previously concentrated for the manufacture of common salt. The mother liquor contains a small percentage of common salt along with magnesium chloride. On further concentration of the liquid and cooling it a few degrees below 0°C . a reaction sets in with the formation of Glauber's salt.

MANUFACTURE.

I

The major portion of the sodium sulphate in a very impure state is manufactured as a bye-product in the manufacture of hydrochloric acid from common salt and sulphuric acid, in cast iron cylinders and in glass retorts. Here hydrochloric acid is the principal product and the bye-product called salt cake is an impure form of Glauber's salt.

It is manufactured by treating the common salt with the requisite amount of concentrated sulphuric acid, i.e., for every 50 parts by weight of common salt 60 parts of acid may be used. The mixture is heated in a cast iron pot on the bed of a reverberatory furnace for several hours when a fused mass known as salt cake is obtained. The mass is next treated with hot water and the solution

thus obtained is concentrated when crystals of sodium sulphate begin to appear. This hydrated salt readily gives out its water which is retained by it in forming crystals, and falls to an opaque powder.

The reactions involved in the preparation of the Glauber's salt are



The reactions can also be carried out by heating the mixture of salt and sulphuric acid either in an open Roaster or in a muffle or close Furnace, which are explained under hydrochloric acid.

II.

Sodium sulphate is also obtained as a bye-product in the manufacture of carbon dioxide (for soda water), which is prepared by treating sodium carbonate with sulphuric acid. Large quantities are also obtained as a bye-product in saltpetre refining in Bihar or residue in the manufacture of nitric acid from Chile saltpetre.

PURIFICATION.

When pure sodium sulphate or Glauber's salt is to be made from the impure salt cake, this purification is always performed by dissolving, precipitating the impurities, separating the liquor from the precipitate, and obtaining the desired product from the solution.

The preparation of pure crystalline Glauber's salt is considerably easier than the preparation of the anhydrous salt. The crude salt cake is dissolved in water heated by open steam in lead-lined wooden vats. The free acid present is neutralised. The iron that always exists in salt cake is oxidised with bleaching powder and

precipitated by means of lime. The flocculent brown precipitate produced by the addition of lime and bleaching powder is allowed to settle and the clear liquor drawn off by means of lead syphons. The sludge is washed and the washings used to dissolve the next batch of salt cake. The clear liquor is then allowed to crystallise by cooling in flat lead-lined tanks.

If the liquor obtained from salt cake in the way described is evaporated at a relatively high temperature, anhydrous sodium sulphate is obtained in place of Glauber's salt. Anhydrous sodium sulphate offers considerable advantages over Glauber's salts in respect of packing and freight. Ordinary Glauber's salt contains over 50 p.c. of water.

PROPERTIES.

Glauber's salt is obtained in large, colourless, monoclinic prisms, which effloresce in the air and fall to an opaque white powder. It readily forms super-saturated solutions which crystallise suddenly when a small crystal of the salt is dropped and the solidification is accompanied by a rise of temperature. The sulphate has the formula of $\text{Na}_2 \text{SO}_4, 10 \text{H}_2\text{O}$.

Glauber's salt is largely used as a mordant in dyeing. It has also got some uses medicinally.

CHAPTER IX.

PLASTER OF PARIS.

SULPHATE of calcium or Gypsum is sold in the form of crystals or of powder, as plaster. Gypsum is found in abundance in salt mine of Khewrah State in the Punjab. Crystallized gypsum is a hydrated sulphate of lime which contains in pure state, 31.86 per cent. of lime and 46.51 per cent. of sulphuric acid, which is only given off at a high temperature.

Plaster of Paris is chiefly noted for its "setting" properties. It is largely used as a medium for making models and moulds. Sulphate of lime (plaster of Paris, Gypsum) can be used for pottery ware fired at a high temperature, because it is only decomposed with great difficulty. Its only advantage is its solubility in water, which allows it to be mixed more easily in pottery ware.

PROCESS OF MANUFACTURE.

Plaster of Paris is manufactured by heating gypsum at a temperature of 120° to 130°C (248° to 266°F). This must be done out of contact with fuel, as the local heat of the burning particles that would be mixed with the gypsum (1) causes complete dehydration to calcium sulphate which is not plaster of Paris, and (2) allows of the reduction of calcium sulphate to calcium sulphide where gypsum is in direct contact with carbonaceous matter. The gypsum is piled over arched fireplaces, either in a rectangular chamber or in an egg-shaped kiln. Good plaster corresponds with the formula 2CaSO_4 .

H_2O , complete dehydration only occurring at 194°C (381°F), when calcium sulphate (CaSO_4) which is but slowly acted on by water, is obtained.

USES.

Plaster of Paris is largely employed for its "setting" properties as a medium for making models and moulds.

The mechanism of its setting may be understood from the following facts:—

When plaster of Paris is shaken with water, some of it is immediately dissolved. This portion then combines with water and is reconverted into gypsum which is less soluble than plaster so that crystals of the hydrated salt are deposited, and more plaster is dissolved by the same water. The process repeats itself until the whole quantity of calcium sulphate has crystallised out in the form of gypsum. Obviously, when the water is only sufficient to make a cream or paste with the plaster, this cycle of reactions will convert the paste into one composed of crystals of gypsum, which being needle-shaped and interlaced constitute a coherent mass. Theoretically, about 13 per cent. of water, reckoned on the weight of the plaster, is necessary for its setting but in practice at least 35 per cent. of water is used, as otherwise the setting is unmanageably rapid. Anhydrous calcium sulphate will set when mixed with water, but more slowly than plaster of Paris, becoming much harder than the latter.

CHAPTER X.

HYDROCHLORIC ACID.

LIKE sulphuric acid, hydrochloric acid is another important mineral acid employed in various arts and industries, namely for the production of chloride of lime, potassium chlorate, and other chlorine preparations (e.g., chloral hydrate, chloroform, chloro-benzyl, benzotrichloride, methyl chloride); it serves also in the manufacture of sal-ammoniac, antimony chloride, glue, and phosphorus; in the production of carbon dioxide (for mineral waters) in the manufacture of alizarine, resorcin, and salicylic acid, in the preparation of sodium bicarbonate, in purifying bone black for sugar works; in bleaching as a substitute for sulphuric acid; in converting saccharose into a fermentable invert-sugar; in the production of ammonia and methyl chloride from the dregs of best treacle; in the metallurgy of copper, nickel, cadmium, zinc, and bismuth; for dissolving metals (tin), either alone or when mixed with nitric acid as aqua regia; for purifying sands for the glass manufacture; for carbonising wool. An important use of hydrochloric acid occurs in the cotton manufacture, i.e., for decomposing the lime soap which is formed when cotton tissues are impregnated with fatty matters. Its principal use in India is likely to be for the manufacture of zinc chloride.

METHOD OF PREPARATION.

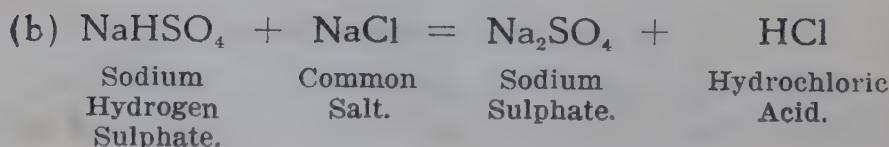
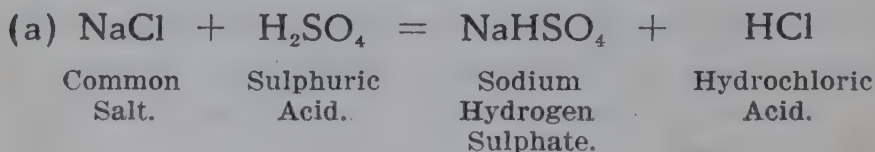
Hydrochloric acid is a gas and is made by heating sulphuric acid with common salt. The gas evolved is

absorbed in water and this forms what is commercially known as hydrochloric acid containing about 33 per cent. of the actual acid. The residue left in the still is known as salt cake and consists principally of sodium sulphate. In other countries salt cake is an important article of commerce, being used for example in large quantities in the manufacture of glass but in India it has up to the present proved nearly or quite unsaleable. It is however used at present in small quantities in the manufacture of Glauber's salt and sodium sulphide. Hydrochloric acid can also be made by the direct combination of hydrogen and chlorine, which are obtained as bye-products in the electrolytic manufacture of caustic soda.

Hydrochloric acid is generally manufactured by the action of sulphuric acid on common salt. This method being the oldest is still adopted in many factories as no better method than this has yet been invented. The process may be represented by the equation:—



But as actually carried out it takes place in two stages, according to the following reactions:—



These reactions may be carried out by heating the mixture of common salt and sulphuric acid either in an "Open Roaster," or in a muffle or "Close Roaster."

OPEN ROASTER.

The open roaster consists of two parts, namely the cast iron pan (A) and the reverberatory hearth (C). The common salt (sodium chloride) and sulphuric acid of 100 gr. 1.72 are put into the pan (A) and are moderately heated by a fire on the grate (E). The first reaction commences at a comparatively low heat and the gaseous hydrochloric acid escapes through an earthenware pipe (B) just over the pan and makes its passage into the condensing vessels. When the first reaction is finished, the fused mass of acid sodium sulphate and unreacted salt is raked up on the reverberatory hearth (C) so as to expose it to the high temperature of the flame from (D). This completes the reaction, and a pasty mass of normal sodium sulphate is formed. The hydrochloric acid vapours, set free during the chemical change, mix with the furnace gases from (D) and pass out through an outlet (F) into the absorbing apparatus, a description of which will be treated later on. The furnace gases are contaminated with the acid vapours to such an extent that a very concentrated solution of hydrochloric acid cannot be produced with the open roaster; however, it yields acid strong enough for use in many industrial purposes. Moreover, the soot and dust from the furnace at (D) mix with the acid, and may cause clogging in the passages and pipes of the absorption apparatus. In spite of these disadvantages the open roaster has the advantage over

the close roaster that it yields more sodium sulphate with less consumption of fuel.

MUFFLE OR CLOSE ROASTER.

The muffle or close roaster yields stronger and purer acid than that produced by the open roaster. The pan (A) is constructed very much similar to the open roaster, but it is heated by the furnace gases from the grate (D). The acid vapours produced in the pan escape by the pipe (C) to the absorption apparatus. The muffle (B) is made of fire-clay or brick, and is heated by the flames from the grate. The mixture of sodium sulphate and salt is raised from the pan into the muffle, when it is heated to a red heat and the acid vapour liberated passes through the pipe (E) to the absorption apparatus. In this form of roaster the acid and dust from the grate are kept away from the pan vapour, and a concentrated acid vapour is obtained which favours the formation of a concentrated solution of hydrochloric acid in the absorbers. But the muffle roasters are expensive to build, yield a smaller output of sodium sulphate and require more fuel than the open roaster. Moreover they often crack, thus allowing acid vapour to escape into the flues and chimney, causing loss of acid and creating a nuisance.

DESCRIPTION OF THE PAN.

The roasting pan (A) in both furnaces is about 4 feet in diameter, 7 inches thick at the middle and 4 inches at the sides. It is made of cast-iron and is placed at one end of the reverberatory furnace. After a charge is drawn, the pan is cooled somewhat before introducing another, for cold salt coming in contact

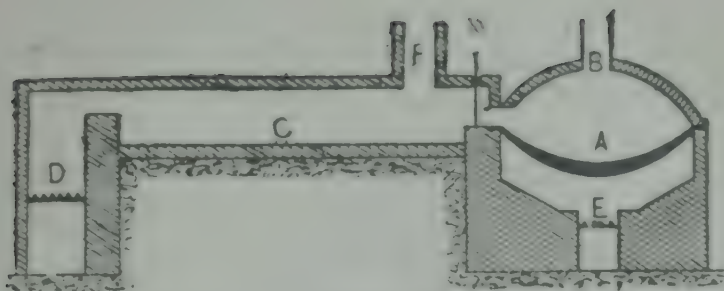


FIG. 6. OPEN ROASTER.

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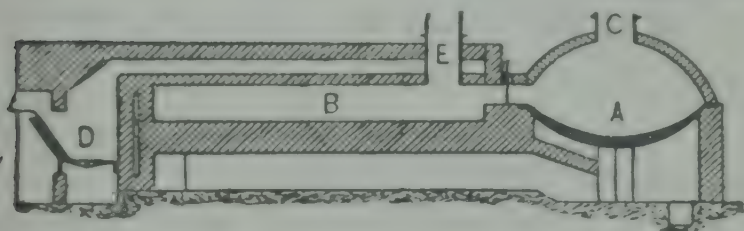
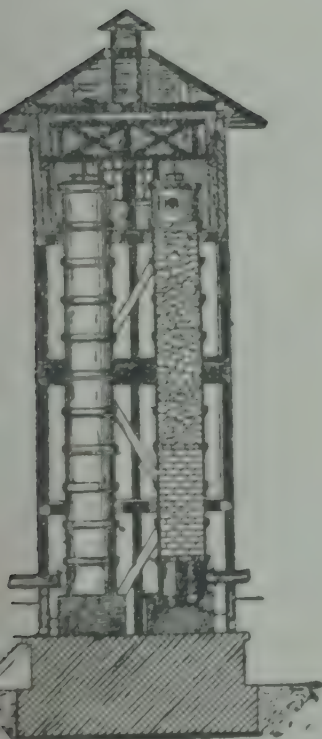


FIG. 7. MUFFLE OR CLOSE ROASTER.

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8. ABSORBING TOWER.

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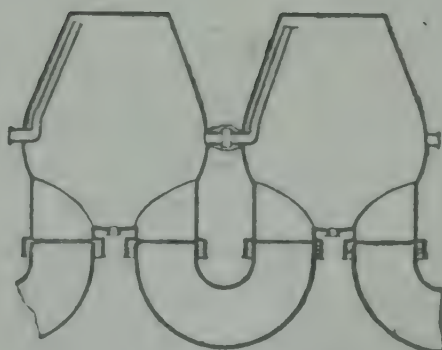


FIG. 9. WOULFF BOTTLE.

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hot pan might crack it. The sulphuric acid is generally heated to 100° to 130°C for the same reason.

MECHANICAL FURNACE.

In these furnaces stirring is done by mechanical stirrers. Mactear's revolving furnace is a modern type. It consists of an arch in which a circular bed revolves driven by a gearing mechanism. The mass moves towards the circumference when it gets intimately stirred and is subjected to greater heat.

CONDENSING APPARATUS.

The hydrochloric acid gas is absorbed in water, by passing through tall towers (Fig. 8) filled with coke through which water trickles; or in a series of large earthenware Woulff bottles (Fig. 9) with an absorption bottle at the end to catch acid gas which may pass through the bottles. These are set encascade and the tubulatures joined so that a stream of diluted acid in the tower flows through them in opposite direction to the movement of the gas.

MANIPULATION.

During the second reaction, the charge is constantly stirred with a "rabble," a large hoe-shaped tool, to prevent "sticking" or burning on to the hearth or retort. The stirring is very heavy work and the workmen are sometimes careless, and allow a crust to form, which may crack and shuffe. Hence, many attempts have been made to construct mechanical stirrers. Of these, the Mactear furnace is the most successful, but the difficulty of protecting the stirring mechanism from the acid fumes, and the cost of building and heavy up-keep charges, have caused general abandonment of mechanical furnaces.

CONDENSATION.

The condensation of hydrochloric acid vapour is so simple a process as it at first appears. The gases from the roasters are very hot, and must be cooled if they can be absorbed to form a strong acid. Moreover, with open roasters, there is a large amount of air present (nitrogen and carbon dioxide from the fire) which dilutes the acid vapours. Then, too, the vapours are set free regularly in any roaster, there being a rapid liberation during the progress of the first reaction, and a slower liberation during the second. This may cause a temporary rush of vapours through the apparatus, so that they cannot be properly taken up by the water.

PROBLEM OF ABSORPTION.

Hydrochloric acid evolved from the pan (pan gas) is cooler and more concentrated and hence more easily condensable than that evolved from the hearth of a roaster (roaster gas). So the two gases are sometimes separately condensed. This does not arise in the case of a mechanical furnace.

The absorption of hydrochloric acid gas in water is not so easy and simple as it appears at first. The difficulties to overcome are the variation in the concentration of hydrochloric acid in the gas, the variation in temperature of the gas escaping from the furnace and the highly corrosive nature of both the gas and the acid. Another important factor is the evolution of considerable amount of heat (650-850 B.Th.U. per lb. of HCl) during the absorption of hydrochloric acid in water which has an adverse effect upon the solubility of the acid. For efficient absorption a special cooling arrangement is necessary to effect efficient absorption. This is, in fact, achieved during

passage of the gas through a long conducting pipe prior to its absorption.

CONDUCTIVE PIPE.

These pipes are generally 12-15 inches in diameter and are made of stone-ware or unglazed fireclay boiled in tar. Water cooled glass pipes are also becoming increasingly favourite and if properly handled stand better than the earthenware pipes. But in most cases cast iron pipes (9 ft. long, 2-2½" in diameter and 1" thick) jointed together from the conducting pipe are used. The conducting pipe rises perpendicularly from the furnace and gradually slopes down towards the base of the absorption tower. For economy of space, the conducting pipe may rise and fall perpendicularly before being connected to the tower while in some cases the rise and fall are inclined at an angle of 60°. The temperature of the gas inside the cast iron pipe is not allowed to fall to such an extent as to effect condensation of the acid in the pipe. In practice the hot gas travels at first through the iron pipes and as soon as the temperature falls to the critical point, the metal pipe is replaced by earthenware pipe. The total length of the conducting pipe varies from 80-120 ft. or even more.

SCRUBBING THE HYDROGEN CHLORIDE.

To remove the sulphuric acid vapours that have been carried along with the hydrochloric acid gas, 3-6 stone cisterns are interposed between the furnace and the absorption tower. In other cases empty or packed towers filled with water just sufficient to saturate the gas with water vapour are preferred for the removal of sulphuric acid.

ABSORPTION OF THE HYDROCHLORIC ACID GAS.

An important condition for good absorption is the gas-liquid interface offered per unit volumes of the gas per unit of time. Various types of absorbers are used for this purpose. The most common form is the earthenware or stoneware Woulff-bottles reference to which has been made on page 77.

Another type of absorber, called Fansted absorber, is made of a phenolic plastic re-inforced with asbestos fibre in the upper part of which is placed a tangent condenser. The heat liberated by the absorption of acid in one part of the absorber causes evaporation of water in the lower part. This condenses as weak acid in the upper part which refluxes back downwards, the concentrated acid being finally withdrawn at the bottom.

But these devices are effective in case of rich gas containing about 50% or more hydrochloric acid. If the percentage is lower, the absorption is carried out in column or plate towers in conjunction with a series of Woulff-bottles.

Absorption by Woulff-bottles alone is suitable only for small or medium sized works. In large works they are used as accessories to coke towers. The coke towers are made of sandstone fire-bricks, earthenware or even wood. The towers are square or hexagonal in shape, 5-120 ft. in height and 9-64 sq. ft. in area according to the capacity of the furnace. The foundation is very carefully laid with a melted mixture of pitch and brimstone followed by a layer of sandstone and silicious cement. A wooden frame is constructed upon this foundation to support the towers. The bottom stones of the tower are thicker (7" or more) than the top ones (about 5"). Inside the tower is a grating made of best fire brick upon which is laid a loose

packed layer of best and hardest quality of oven coke of 5"-6" in size, gradually diminishing to about 2" at the top. In some cases the irregular coke is replaced by uniformly shaped earthenware pieces having uniform interstices but nevertheless, the coke packing is still found to be in great favour. In the top of the tower is placed a tank from which water is uniformly distributed over the packing by means of a turbine distributor. The gas enters at the base and during its upward travel through the packing meets the downward current of water and is absorbed. The weak acid thus produced is removed through an outlet at the base and is made to pass through a series of Woulff-bottles counter-current to the gas from the conducting pipes. The concentrated acid (specific gravity about 1.20) is finally withdrawn from the 1st bottle in the series. In some works, plate towers have replaced the coke towers for condensing the acid.

HARGREAVE ROBINSON'S METHOD.

In this method a battery of cast iron cylinders connected in series and arranged in two rows of 5 in. each, constitutes the furnace. The cylinders are about 12 feet in height and 18 feet in diameter, fitted in brick works and are heated extremely by coke from the fire place provided with each cylinder. The optimum temperature is 500°C . and the chemical action is accompanied with considerable evolution of heat. So, in practice, the first and last of the series are heated, the chemical action is maintained in the intermediate cylinders which are sometimes required to be cooled to prevent the rise of temperature which may disturb the efficiency of production.

OPERATION.

Salt pressed in the form of briquettes is packed in these cylinders and sulphur di-oxide obtained from the burning of pyrites, mixed with about equal volume of air and some steam is made to pass through the cylinders in succession. The hydrochloric acid gas generated is carried along with the sulphur-dioxide current. The rate of chemical action being slow, the gases are kept in contact with the salt for a considerable period. A cylinder containing 40 tons of salt requires 15 to 20 days continuous action to secure complete concentration. When no further absorption of sulphur dioxide is observed in a cylinder, it is cut off from the series emptied and refilled with salt briquettes. This cylinder is then made the last in the series so that the fresh charge is exposed to nearly exhausted sulphur fumes. The spent gases are exhausted from the last cylinder of the series through earthenware pipe and the HCl gas present to the extent of about 10% by volume is condensed.

The method of absorption of the acid is the same as described above.

SYNTHETIC HYDROCHLORIC ACID.

The constantly increasing production of electrolytic chlorine has led to the synthetic production of hydrochloric acid. In the Castner process of caustic soda manufacture from brine solution, hydrogen and chlorine under identical conditions of pressure and temperature are led into a chamber through a V-shaped tube and burnt with the production of a constant stream of hydrochloric acid. Instead of using the V-tube, the hydrogen gas may enter a cylindrical box from which it issues through several burner nozzles arranged in a circle. Surrounding this is

her containing several nozzles for leading in chlorine into the space. Hydrogen gas is first ignited and the initially present is replaced by chlorine, thus making it to burn in an atmosphere of chlorine gas. The fumes of hydrochloric acid gas produced is led through a series of silica tubes, cooled externally by a constant circulation of cold water and absorbed.

PURIFICATION.

The ordinary muriatic acid of trade is an aqueous solution of hydrochloric acid vapour, having a specific gravity about 1.20 and containing about 40 per cent. by weight of hydrochloric acid vapour. It is impure, containing sulphuric acid, iron, iron chloride, arsenic, and generally, lead and barium chlorides. Its yellow colour is partly due to organic matter, and sometimes to iron and free chlorine. To remove arsenic and sulphuric acid, the acid is diluted to 1.10 sp. gr., and barium sulphide is added; a pure hydrochloric acid vapour is then driven out by distillation and absorbed in pure water. Or, a solution of stannous chloride in concentrated hydrochloric acid is added to the impure acid, which latter must have a strength of at least 1.10 sp. gr. A brown precipitate of arsenic with some tin compounds is formed and is removed by decantation. Sulphuric acid is removed by adding barium chloride and redistilling. To remove chloride, the crude acid is digested with shavings of copper for some hours. This precipitates arsenic, and the chlorine combines with the copper. The acid is then redistilled.

CHAPTER XI.

COMMON SALT & MAGNESIUM CHLORIDE.

COMMON salt (sodium chloride), a food for human and animal consumption, now plays a very important part in industry. It may be regarded in itself as a base industry, as various other substances used in daily work are derived from it.

The four important groups to which the salt finds its use, besides human consumption are: (1) the manufacture of Hydrochloric Acid, (b) the manufacture of Soda Ash, (c) Refrigeration, and lastly (d) Electro-Chemistry. Every group, except Refrigeration, has again its sub-groups. Besides these, salt is used for several other miscellaneous purposes, viz. as a condiment for the preservation of meat, fish, etc. and also for producing a glaze on common earthenware and for the soaps and many other industries as well.

SOURCES OF INDIAN SALT.

The salt produced in India is derived chiefly from various sources, viz. from sea-water, from sub-soil water and lakes in areas of internal drainage, and from rock salt beds. By far the larger amount, about 60 p.c., is derived from the first source, chiefly in Bombay and Madras while the rock salt beds of salt range, of Kohat and Mandi State provide about one tenth of the Indian output. Sea-salt is also obtained from areas at the mouth of the Indus. In Bombay and Madras sea-water is pumped into shallow pans on the sea-coast, and evaporated by

ar heat to manufacture salt. In Madras Presidency, small amount of salt is collected in Masulipatam area, the rest is manufactured from sea-water. In Upper Burma, it is obtained from sub-soil brines notably in the districts of Sagaing, Shwebo, Myingyan, Meiktila, and Manipaw State. The most important areas worked for sub-soil and lake brine is the desert region of Rajputana. From which about 250,000 tons are annually produced. The Rajputana supply chiefly comes from the Sambhar Lake, where brine is extracted and evaporated by solar heat. The total products of Sambhar salts average annually 205,269 tons. In the Lesser Runn of Cutch, the brine is also evaporated by solar heat and the product is known as Baragara salt. The whole of Rajputana is impregnated with salt, extending from the coast of Cutch and Sind North, and north eastwards to the borders of Delhi District and Bahawalpur State. The Salt Range mines (in the Punjab) contain an inexhaustible supply. They are worked in chambers excavated in salt strata, some of which are 250 ft. long, 45 ft. wide and 200 ft. high.

In Bengal, the damp climate together with the large volume of fresh water from the Ganges and the Brahmaputra flowing into the Bay of Bengal renders the manufacture of sea salt difficult. An investigation by the Industries Department, Bengal, on the comparative prospects of salt raising on Bengal, Orissa and Madras seacoasts shows that Madras is the most suitable place for salt raising, the rainfall being completed during a short period, the relative humidity being low during the dry season, and there being no disturbance from the influx of fresh water streams. Vizagapatam stands next in merit. Regarding Balasore and Berhampore, the condi-

tions are said to be much worse than those of Madras and Vizagapatam, while in the case of the Saugor Island which represents Bengal coast, the conditions are most unfavourable, if not absolutely prohibitive.

It may be mentioned here that in manufacturing salt from sea water by solar heat, three factors are to be taken into consideration: namely, the rainfall, humidity and latitude. A hot place with scanty rainfall and low humidity is most likely to be the most satisfactory for salt making.

MODES OF PREPARATION.

To manufacture salt from sea water, a piece of flat land well above the high-water level of the sea is selected. (Fig 10.) The land is then levelled and walls are made on all sides. The whole shallow space is then divided into a series of compartments by internal walls. Sea water is admitted into the first at high tide in spring and is allowed to stand there to get concentrated by solar heat up to 25°Be . Crystals of calcium carbonate and gypsum are deposited in this pond. Then the liquor is run into the adjacent tank. When the liquor attains 27°Be , crystals of salt are deposited in the bottom of the tank. The mother liquor is then transferred into a third adjacent reservoir where concentration is allowed to proceed up to 32°Be . Here salt of inferior quality is obtained.

The separated salt is heaped in another place to dry where magnesium chloride is washed out by occasional rain.

SALT BY DIRECT BOILING PROCESS.

In case of sub-soil salt water, this may be pumped out and then made into salt by solar evaporation as above.

Salt may also be manufactured by direct boiling of brine obtained from the sea, lake or salt springs. Evaporation is carried on in big iron pans made of sheets riveted together. The temperature is raised to 130° to 140°F. As the brine concentrates, crops of salt are deposited. These are then separated from the mother liquor.

SALT FROM SALINE EARTH.

Salt may also be obtained from saline earth by (1) washing saline earth, (2) lixiviating it in water and filtering the solution obtained for getting rid of clay, sand, etc. and (3) concentrating the solution by direct heat.

GENERAL PROCESS OF SALT MANUFACTURE IN BENGAL.

Sea-brine from tidal estuaries and canals is trapped in creeks and channels every spring tide. It is then elevated to the first of a series of condensers which is then run by gravitation through three other sets of condensers where the brine progressively increases in density by solar evaporation to approximately 25°Be. , i.e., the saturation point at which calcium sulphate or gypsum begins to be deposited and the deposition of common salt commences. The dense brine is then run into a storage tank ready for separation of salt by either process. Rain water falling on the surface of this saline tank remains on top in a distinct layer owing to its lower specific gravity and is run out from the reservoir by a drain on the top leaving the saline portion unaffected.

THE BURMA PROCESS.

From a sump in the storage tank a pipe leads the brine into a well inside the factory. The brine is thus drawn off from the bottom of the tank and is lifted from

the well by buckets and is poured on the pans set over a furnace where it is boiled until sodium chloride (common salt) is deposited. Some conservation of heat is secured by applying heat direct to only 1/6th portion of the surface, the flue passing through the rest before escaping from the chimney thereby heating to some extent the distant part of the pans without additional cost.

The salt is then removed from the pans as soon as formed and put into bags which are placed on ashes in shade to drain the moisture and dry the salt.

SOLAR EVAPORATION PROCESS.

From another sump in the storage tank a pipe leads the brine to a well inside the first series of condensing beds of cement concrete. The brine is lifted from the well by buckets and poured on the crystallising bed to a depth of about one inch which is evaporated by solar heat for a whole day or until a layer of salt crystals, generally 1/8th of an inch thick has formed. This salt is removed almost every afternoon and placed in bags and allowed to drain and dry on ashes in shade as in the former process.

There have been two contrivances for letting the concentrated brine make its way into the reservoir in case of rains and letting the rain water escape by a different channel after the rainfall so that no concentrated brine be washed or the bed remains unutilised for any time of actual rainfall.

ACTUAL WORK.

In this connection a description of the actual working of Dadanpatra factory of the Bengal Salt Co. will be illuminating.

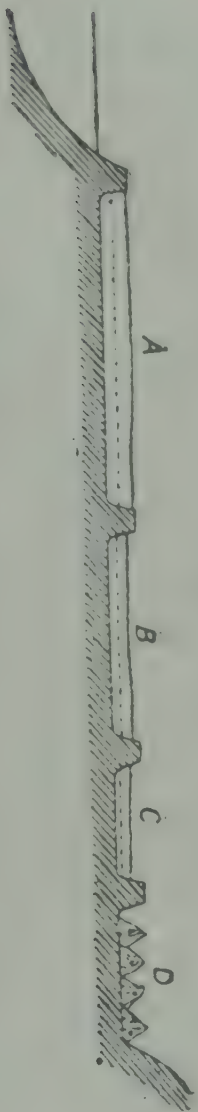


FIG. 10. SALT FROM SEA WATER.

A—1st. compartment where sea water is admitted at high tide.

B—Crystallising pond.

C—Pan for inferior salt.

D—Separated salt raked together into heaps.

Salt is being manufactured here from brine by (a) solar evaporation alone, and (b) solar evaporation followed by boiling and also (c) from scrapings of saline earth followed by lixiviation and boiling. Work with brine is not carried on during July-October, when the strength of brine is very low and solar evaporation inconvenient. The strength increases from November and it is about 2°Be. in December. Thereafter it rises and reaches 3°Be. at which it remains up to June. The strength is higher by about $\frac{1}{2}^{\circ}\text{Be.}$ for 4 days in the fortnight—from the 5th to the 8th day of the moon and full advantage of this higher strength is taken.

The entire low land surrounding the salt works is inundated during the fortnightly high tide. The daily high tide, however, brings sea water within close reach and fills a reservoir tank 100 ft. \times 100 ft. \times 5 ft. (with high banks and arrangement for admitting sea water). From the reservoir the water is lifted by means of swing baskets and led through channels into shallow kuchcha troughs called "condensers." The condenser consists of a bed carefully levelled and enclosed by thoroughly rammed earthen walls about $1\frac{1}{2}$ ft. high and 2 ft. wide. The condensers are constructed at different levels so that gravity helps the water from one condenser to pass into the next on opening a passage. The brine lifted from the reservoir passes in succession through 3 condensers and reaches the 4th which is at the lowest level. In each condenser brine is concentrated by solar evaporation.

The concentration taking place is stated to be of the following order.

- Condenser No. 1—Strength increases from 3°Be. to 6°Be.
- Condenser No. 2—Strength increases from 6°Be. to 10°Be.
- Condenser No. 3—Strength increases from 10°Be. to 18°Be.
- Condenser No. 4—Strength increases from 18°Be. to $22\text{--}24^{\circ}\text{Be.}$

The concentrated brine from the 4th condenser is lifted by means of a hand pump and led into a cement plastered reservoir tank (A), 60 ft. \times 30 ft. \times 5 ft. The strength of brine at "A" was found to lie, on the date of visit, at a sp. gr. of 1.190 at 100°F (22°–23°Be.).

The brine from tank "A" is delivered (1) to salt beds or (2) salt boilers. The delivery is at present effected by means of buckets but a hand pump is being fitted up. The salt beds consist of cement plastered shallow troughs 50 ft. \times 25 ft. in which the deposition of salt takes place by further concentration of the brine by solar evaporation. The product is salt of the Karkach kind. The mother liquor containing a large proportion of magnesium sulphate is led out and reserved in a pool. It is possible to recover magnesium sulphate from this liquor.

The brine delivered from "A" to the boiling section is concentrated in salt pans by coal fire. The product is salt of a fine grain and very fair colour.

For solar evaporation the company has the following 'condensers,' and 'salt-beds' (cement plastered):—

Condensers	No. 1—350' \times 150' (in 2 parts).
Condensers	No. 2—330' \times 150' (in 2 parts).
Condensers	No. 3—325' \times 60' (in 2 parts).
Condensers	No. 4—325' \times 50' (in 2 parts).
Salt beds	No. 1— 50' \times 25' (in 2 parts).
Salt beds	No. 2— 50' \times 25' (in 2 parts).
Salt beds	No. 3— 50' \times 25' (in 2 parts).
Salt beds	No. 4— 50' \times 25' (in 2 parts).

It is interesting to note that salt could be produced by solar evaporation even in winter. The production of 40% of the total output of the salt by solar evaporation has reduced the average cost of manufacture appreciably and placed the company in a favourable position to compete with the imported salt in the market.

FISHING SALT.

Fishing salt made for the fishing industry is a coarse grained variety of salt made by crystallising at $38-60^{\circ}\text{C}$ in large pans, often 60 ft. long, 25 ft. wide and 2 ft. deep. The salt is removed weekly or fortnightly. The longer the salt remains in the pans, the coarser the grain. A little alum added to the brine favours the formation of large hard crystals.

BAY SALT.

Bay-salt is still coarser in grain than fishing salt, the pans being very large, sometimes 135—140 ft. long, 30 ft. wide and 2 ft. deep. The brine is kept at $40-50^{\circ}\text{C}$ and the salt is drawn from the pan every 3 or 4 weeks.

HOPPER SALT.

It is made by adding alum to the salt, when the salt crystallises out in hollow cubes which float about before they sink to the bottom of the pan.

CLEANING THE PANS.

Various impurities gradually separate out on the pan and form a scale over the bed of the pan. Loss of efficiency occurs therefrom. To avoid this periodically all the liquid is run away and the pan cleaned and scale removed.

MAGNESIUM CHLORIDE.

The brines as treated by solar evaporation for the production of common salt contain a considerable proportion of magnesium chloride besides a notable amount of magnesium bromide. It was estimated by the Indian Munitions Board that 193,000 tons of magnesium chloride, 27,000 tons of magnesium sulphate, 20,000 tons of

and evaporate until a portion of the liquid, withdrawn on the end of a glass rod and cooled, forms an opaque white solid. Pour it out now into proper moulds, and when the salt has solidified, but before it has cooled, place it in closely-stoppered bottles.

PROPERTIES.

Zinc chloride, when pure, is a colourless amorphous mass or crystals; generally a whitish-grey, semi-transparent mass, having the consistence of wax; fusible at 100°C ., volatile at a strong heat, condensing in crystals; freely soluble in alcohol, ether, and water, highly deliquescent; coagulates albumen and gelatin, and corrodes animal substances.

Dry chloride of zinc is chiefly used as a caustic. It is also employed on a large scale in 'weighting' cotton goods. When a solution (sp. gr. 1.7) is boiled with an excess of oxide, a liquid is obtained which possesses the property of dissolving silk; this is used for separating silk fibres from those of wool, cotton, or linen, all of which dissolve in normal zinc chloride. Zinc chloride is a powerful antiseptic and disinfectant and is used as a preservative in the preparation of office paste.

GOLD CHLORIDE.

The most convenient way of preparing the chloride of gold, strictly speaking, trichloride of gold, is to dissolve gold in aqua regia mixture consisting of 1 part of nitric acid and 2 parts of hydrochloric acid by volume. To dissolve 1 ounce of gold (troy weight) about 4 ounces of aqua regia will be required, but this will depend upon strength of the commercial acids. The best way of preparing this compound is to carefully place the required

quantity of gold in a glass flask and add the calculated amount of aqua regia. Soon after the mixed acids have been poured on the gold, gas is evolved, and the chemical action may be accelerated by placing the flask upon a sand-bath moderately heated.

It is always advisable, when dissolving this or other metal, in order to avoid excess of acid, to apply less of the acid than the maximum quantity in the first instance, and, when the chemical action has ceased, to pour off the dissolved metal and then add a further portion of the acid to the remainder of the undissolved metal, and so on until the whole is exhausted.

The solution of chloride of gold is to be carefully poured into a porcelain evaporating dish and this, placed in a sand-bath, is gently heated until all the acid is expelled, when the solution will assume a reddish hue. The residue is next dissolved in small quantity of distilled water and crystallised.

Gold chloride is employed as a substitute for mercury, in scrofula, chronic skin diseases, tuberculosis, etc. Its most important use however is as a reagent in photography, large quantities being manufactured for use as a toning agent in toning photographic prints. To some extent it is also used for electro-gilding.

CHAPTER XIII.

CHLORINE.

CHLORINE is largely used as a bleaching agent in the paper and cotton industries. In a liquid form it is employed in the manufacture of synthetic dyes. It also forms the first step in the manufacture of bleaching powder.

PROCESS OF MANUFACTURE.

Chlorine is made from hydrochloric acid (18 to 20 Be) by heating it in stills placed on sandstone or earthenware grid with manganese dioxide by means of a current of steam. The reaction which takes place is represented by the following equation:



In big factories a number of stills may be used instead of one. On a small scale chlorine may be made in earthenware generators.

Manganese chloride, the bye-product in the industry, is re-converted by large factories into manganese dioxide to be used again for the generation of chlorine.

After the completion of the action the chloride liquor is run into a cemented tank provided with a stirring apparatus and a pump. Lime is added here to neutralise the liquid. Thereby iron hydroxide and other impurities are precipitated. The liquid is then pumped into an iron settling tank and thence to the oxidation towers made of iron. Here steam is injected to raise the temperature of the manganese chloride to 55°C and the calculated

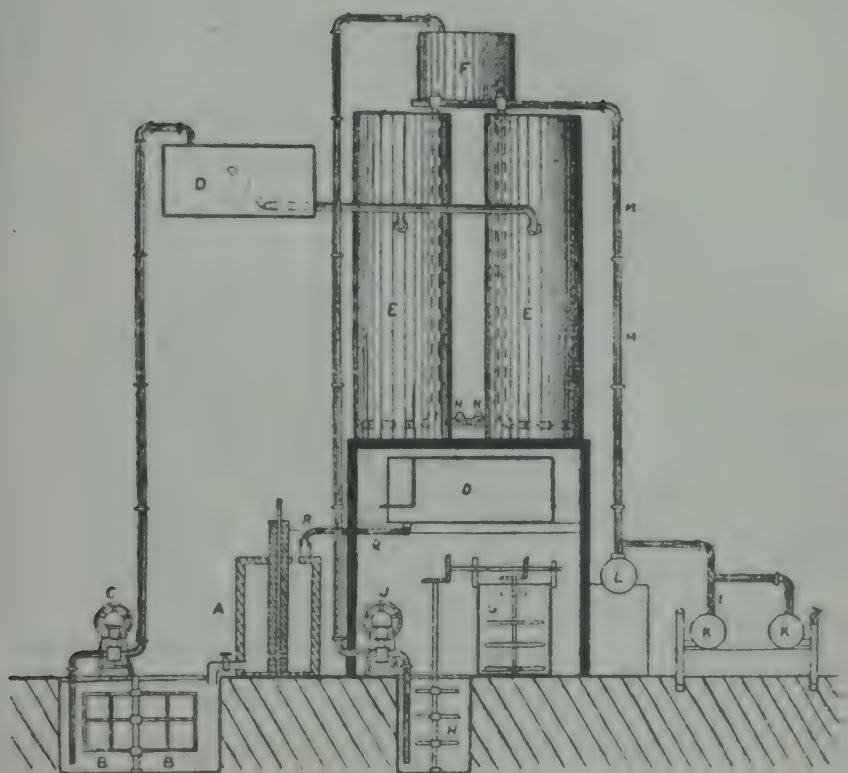


FIG. 11. CHLORINE PLANT.

A—Still.
 B—Cemented Tank.
 C J—Pump.
 D—Settling Tank.
 E—Oxidation Towers.
 F—Lime Tank.
 G—Lime Mixer.

H—Slaked Lime Tank.
 K—Blower.
 L—Air Reservoir.
 HM—Air Conducting Pipe.
 NN—Stop-cocks to remove
 Weldon mud.
 O—Settling Tank for mud.



1. The building is a two-story structure with a central vertical section and a taller section to the right. The central section has a small square element at the top, possibly a chimney or roof section. The taller section has a stepped profile. The drawing is light and appears to be a preliminary sketch on a piece of paper.

2. The building is a two-story structure with a central vertical section and a taller section to the right. The central section has a small square element at the top, possibly a chimney or roof section. The taller section has a stepped profile. The drawing is light and appears to be a preliminary sketch on a piece of paper.

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4. The building is a two-story structure with a central vertical section and a taller section to the right. The central section has a small square element at the top, possibly a chimney or roof section. The taller section has a stepped profile. The drawing is light and appears to be a preliminary sketch on a piece of paper.

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ount of milk of lime is admitted from overhead tank. compressed air is forced into the towers, through perforated pipes at the bottom for 4 to 5 hours. Manganese dioxide is thus obtained. The solution is then run into settling tank where the dioxide settles in the form of mud. The mud may then be conducted into chlorine stills and be used again as before. The process of recovery of dioxide may be repeated.

ELECTROLYTIC PROCESS.

The following method of making chlorine by electrolysis is now coming into greater use.

When an electric current is passed through a salt solution, the positively charged sodium ions pass to the negative electrode (cathode), whereas the negatively charged chlorine ions pass to the positive electrode (anode). Arriving at the electrodes these charged ions give up their electrical charges, and the sodium ions become ordinary sodium, which at once reacts with the excess of water to produce caustic soda liberating hydrogen gas. On the other hand, the chlorine ions, after giving up their negative charges at the positive pole, are liberated as chlorine gas and also remain dissolved in the liquid surrounding the anode. In very dilute solutions, and with high electrical potentials, the water suffers electrolysis; oxygen evolves at the positive pole, and hydrogen at the negative.

DETAILED PROCESS.

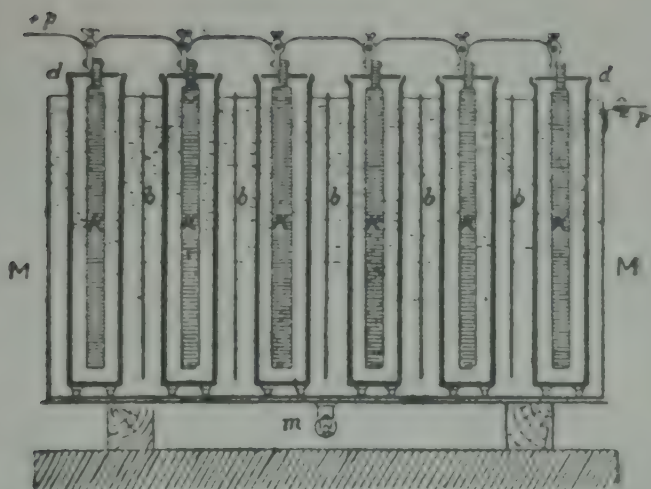
The most satisfactory type of cell employed in this process is that of Griesham, which has been in work since 1900. It consists of an iron box which is made to serve as the cathode. Inside this are placed six small porous

cells serving as diaphragms in which are placed anodes connected in series, the whole being filled with saturated sodium chloride (common salt) solution.

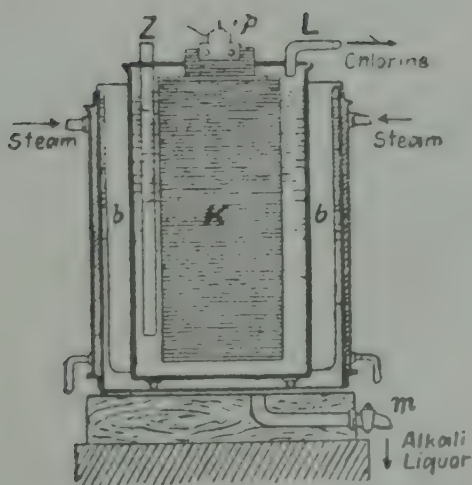
The walls of the small porous cells are composed of cement, sodium chloride, hydrochloric acid. In the use of the common salt it dissolves and leaves an extremely fine-pored wall, which separates the anodic from the cathodic space, and which allows the current to pass through. The anodes dipping into each porous cell are made of magnetic iron oxide fused at a high temperature in electric furnace and poured into moulds. Such electrodes have been superior to the carbon poles previously employed, which are attacked by nascent oxygen. The small porous cells, at the same time, are separated from each other by means of iron plates going right across the main iron box and dipping nearly to the bottom. The iron plates together with the iron walls of the main box form the cathode. The porous cells surrounding the anodes are covered with lids, the chlorine escapes through a tube leading from the interior of the cell. The gas is led away through an earthenware pipe to a collecting chamber.

Each cell is provided with a tube-shaped glass or earthenware for filling in salt, thereby keeping the solution saturated. The bath is also furnished with a tube through which the evolved hydrogen gas escapes.

As the electric current is passed through the saturated salt solution in the bath, the chlorine ion passes into the anodic space and escapes into a chamber where it is absorbed by water forming chlorine water. Sodium ion passes on to the cathodic space outside being converted into caustic soda and hydrogen. As the action proceeds the solution becomes weaker and weaker in strength.



Longitudinal Section.



Cross Section.

FIG. 12. THE GRIESHAM CELL.

d d—Porous Cells.
K—Anodes.

b b—Iron Plate.
MM—Iron Box.

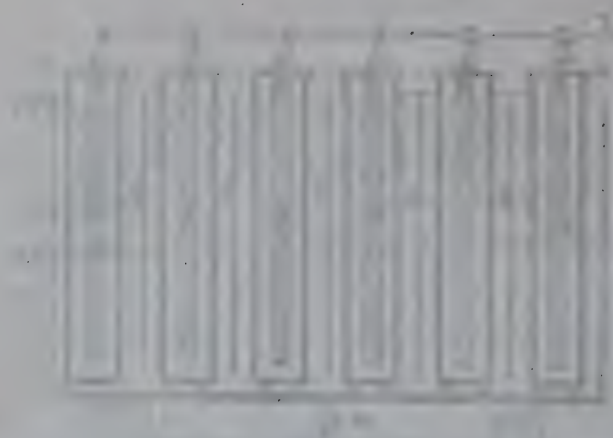


Fig. 1. (a) (b)

Fig. 2. (a) (b)

Fig. 3. (a) (b)

Fig. 4. (a) (b)

Fig. 5. (a) (b)

chloride so that saturated salt solution is run in through pipe and the solid salt added from time to time also maintains the supply of salt to the liquid.

The evolving chlorine is extremely concentrated. It is a greenish-yellow, very irritant suffocating gas. One volume of water absorbs different volumes of chlorine gas at different temperatures:—

Temperature	10°C	20°C	30°C	90°C
Vols. of chlorine	3.095	2.260	1.767	0.380

Moist chlorine is chemically very active and decomposed by sun-light.

CHAPTER XIV.

BLEACHING POWDER.

THE demand for bleaching powder and bleaching materials is very great in India. The manufacture of this commodity on a large scale has been newly undertaken in India. It will be a subsidiary industry to the manufacture of caustic soda by electrolysis. As bleaching powder is unstable and does not keep well in hot climates, it is essential that it should be manufactured locally.

When moderately dry slaked lime is treated with chlorine gas in the cold, it absorbs some 35-36 per cent. of chlorine to form a dry white powder, which possesses strong bleaching and disinfecting properties, and is known as "bleaching powder" or "chloride of lime." These properties arise from its power of giving off the absorbed chlorine again when treated with acids. Although commercial bleaching powder usually contains only 35-36 per cent. of available "chlorine," yet a bleaching powder containing 40 or even 43.5 per cent. of available chlorine is obtained with a slight modification of the process.

GENERAL METHOD OF MANUFACTURE.

In manufacturing bleaching powder of good quality lime—low in magnesia and carbonic acid—must be carefully slaked so as to form slightly moist powder.

This must be carefully slaked so as to form a dry powder containing about 4 per cent. more water than corresponds to the formula $\text{Ca}(\text{OH})_2$. Perfectly dry lime does not absorb chlorine gas at all. The lime should be as pure as possible and to make it into fine powder it is passed through a sieve with 20 to 25 meshes per linear inch before use. The chlorine gas should be cool and dry, and be fully freed from hydrochloric acid gas; it should not contain much carbon dioxide. The presence of a little carbon dioxide in bleaching powder does not matter because carbon dioxide acts on the slaked lime much more slowly than the chlorine. Generally speaking, 64 parts of slaked lime yield 100 parts of 36 per cent. bleaching powder.

The absorption chambers are made of bricks, cast-iron or lead, and are usually $6\frac{1}{2}$ feet in height, and have about 200 square feet of floor area per ton of bleach made each week. Brick chambers are coated inside with tar to make them gas-tight, and to protect them from action of chlorine. The front is covered with asphalted iron plates. The chamber is also provided with windows which allow the interior to be seen.

The slaked lime thus prepared is spread in 3 or 4 inches layer on the floor and shelves of a large chlorine chamber. The chlorine gas either prepared directly or obtained as a bye-product in the electrolytic processes is introduced into the chamber from one end: and opening on the other end allows the air to escape; the flow of the gas is turned off as soon as the chamber is full and at the same time the outlet is also closed. The gas is absorbed by the lime, the surface of which is slaked from time to time. The resulting mass is bleaching powder.

BLEACHING POWDER FROM ELECTROLYTIC CHLORINE BY CHAMBER PROCESS.

The very concentrated electrolytic chlorine is rapidly and energetically on the lime. Hence the chlorine so made, is employed in manufacturing bleach powder, the chamber process, the outline of which is given above may be followed with good results.

The lime is spread in 3 or 4 ins. layers on the floor of a large "chlorine chamber," some 6 or 7 ft. high, 10-20 ft. wide, and 100 ft. long. The walls are made out of tarr or asphalted sandstone slabs (asphalt being very resistant towards chlorine); in modern practice, however, the top and sides are made of sheet lead fastened by straps and timber work, like vitriol chambers. The entrance is covered over with asphalted iron plates. The layer of lime is raked into furrows in order to expose a large surface, and a stream of electrolytic chlorine is led into the chamber from one of the ends of the chamber; an opening in the other end of the chamber allows the air to escape. Two windows allow the interior to be viewed; the flow of chlorine is to be turned off as soon as the chamber is full. The outlet is also closed when the chamber is filled with chlorine. Chlorine enters through a pipe placed at one end near the roof of the chamber. Being a heavy gas it sinks downwards, and is at first rapidly absorbed by the lime; later the absorption becomes slow and the temperature rises, but great care must be taken that this latter never exceeds 25°C . Great excess of chlorine should also be avoided, and so usually a definite amount of chlorine is let into the chamber; the chamber is closed and allowed to stand some twelve to twenty-four hours. In order to expose a fresh surface the lime is turned over from time to time. Finally, before allowing workmen to enter the

chamber and removing the bleaching powder, the last residues of chlorine must be sucked out, either by passing a stream of air, or simply by injecting some finely powdered lime dust.

A chamber making 10 tons of bleaching powder and containing fair excess of chlorine requires some 4-5 cwt. of lime dust blown in through a special fan or distributor. This reduces the chlorine in the chamber to about 0.8 gr. per cubic foot, producing 6 cwt. of extra bleaching powder, and requiring about two hours to settle. Before allowing workmen to enter, the air of the chamber (which should be tested by the works' chemist) should not contain more than $2\frac{1}{2}$ gr. of chlorine per cubic foot. Bleaching powder chambers should have about 200 sq. ft. of chamber space per ton of bleaching powder made per week.

The bleaching powder is then packed into very well made wooden casks (but of hard wood) for transport and storage. The ends are coated with plaster of Paris to prevent access of air, which soon spoils the powder; the casks are stored in a cool, dry place, both rain and sunshine damaging the material.

The yield of bleaching powder is usually $1\frac{1}{2}$ times the weight of the slaked lime.

Since the entry of the chlorine chambers by workmen, and the rake over the surface of lime is injurious for health, and has often been attended by fatal accidents, many devices have been proposed and adopted for minimising the risks. In some forms of apparatus the lime as is laid on perforated shelves of the chlorine chambers, and the raking of the half-finished bleaching powder is entirely worked from outside by mechanical appliances. These attempts do not seem, however, to have been very successful.

MANUFACTURE OF BLEACHING POWDER FROM DILUTE CHLORINE.

The diluted chlorine evolved by the action of hydrochloric acid on manganese dioxide is not suitable for making a good bleaching powder from the chamber process above described, and so an entirely different sort of apparatus is usually employed. It is known after its inventor "Hasenclever's Cylinder Apparatus."

The apparatus consists of six or eight cast-iron cylinders, lying vertically one above the other, of length some 12-20 ft., each provided with a feeding worm which is kept revolving slowly by means of the cog wheels. The slaked lime is poured into the topmost cylinder, and is gradually moved downwards from cylinder to cylinder until it finally escapes from the bottom cylinder. Meanwhile the chlorine gas, freed as much as possible from hydrochloric acid and carbon dioxide, is passed into the bottom cylinder, and streams along in a direction opposite to that of the moving slaked lime, finally escaping at the topmost cylinder by an opening. The chlorine is all absorbed by the lime, and a practically chlorine-free gas escapes at the top opening. The bleaching powder is let out from time to time into a wooden cask situated below. Since chlorine gas might attack the iron work of the spur wheels, the latter are painted with barium sulphate, commercially known as blanc fixe. Each of the cylinders is provided with a number of lids which can be removed when the apparatus becomes blocked up, or when some other disturbance necessitates inspection of the interior of the cylinders.

By this apparatus no danger results to the workmen (as in the chamber process), because they do not come

to contact either with the lime dust or with the chlorine gases. The resulting bleaching powder contains about 35 per cent. of available chlorine. It is packed into very well made wooden casks, the ends of which are coated with pitch to prevent access of air.

CHAPTER XV.

CHLORATE OF POTASH.

THIS important compound, namely, the Chlorate of Potash, has become the object of a pretty extensive manufacture in consequence of its use in the preparation of lucifer matches, as a constituent of white gun-powder and certain mixtures used in pyrotechny, and also as an ingredient in some detonating compound. Moreover, the salt is used in calico-printing and in the preparation of certain aniline colours, while the chemist frequently employs it as a convenient oxidising agent, and as a source of free oxygen gas.

METHOD OF PREPARATION.

Chlorate of potash may be prepared by passing an excess of chlorine gas through a strong solution of potash whereby a mixture of chlorate of potash and chloride of potassium is obtained. The former salt being sparingly soluble in water readily separates out from the latter and can then be collected.

Having made a strong solution of potassium hydroxide with 2 to 3 parts of water a current of chlorine gas is transmitted through it, till it ceases to absorb any more. As long as there is an excess of alkali in the solution "chloride of potash," and chloride of potash alone, is formed; but in subsequent reaction of materials the chloride of potash is converted into chlorate and, as such, is precipitated from the solution. During the first half of the

operation (that is, till the potash is about one-half saturated with chlorine, as indicated by litmus paper ceasing to be darkened and beginning to be blanched), only the chloride of potassium falls. The process should be interrupted at this point in order to remove the potassium chloride settling below, to wash it, to add the washing to the liquor, and then to pass chlorine again freely through the solution. As the operation advances, less chloride of potash is formed, and at length nothing but the pure chlorate of potash is separated in crystals. When, finally, the bubbles of gas pass through without being sensibly absorbed, the process is known to be completed; the liquid may then be allowed to settle, and be poured off from the crystals of chlorate of potash, which are purified from the chloride by dissolving them in three times their weight of boiling water and filtering the solution while hot. On cooling, the chlorate will separate in pearly crystalline plates. It may be rendered quite pure by a second crystallisation.

CHLORATE ON A LARGE SCALE.

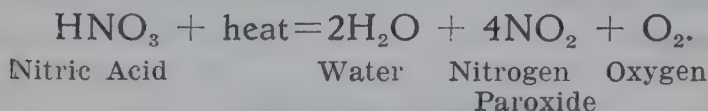
For preparing chlorate of potash on a large scale the following process is now generally adopted.

An excess of chlorine gas is transmitted into a vessel containing milk of lime at a temperature of 120° to 140°F , the liquid being kept agitated by an iron stirrer coated with lead. The reaction between the chlorine and the lime under these conditions results in the production of chlorate of lime and chloride of calcium, with a small quantity of hypochlorite of lime, as represented by the following equation:—



strong nitric acid, the sulphuric acid should be of 92 per cent. strength, and the temperature kept as low as possible during the distillation. The residue consists of a fused mixture of sodium sulphate and sodium hydrogen sulphate and is partly utilised in the preparation of hydrochloric acid and sodium sulphide and partly as chemical fertiliser.

Since the heat of vaporisation of nitric acid is low, the nitric acid vapour is easily condensed. The vapours from the retort contain also nitrogen peroxide due to the decomposition of nitric acid by heat, according to the equation—



The vapours also contain air which leaks into the system owing to the reduced pressure maintained therein. The nitrogen peroxide tends to dissolve in the acid condensed in the condenser and to form nitrous acid. The water formed in the above reaction condenses with the nitric acid. The remaining gases pass into the condenser, tending to carry with them uncondensed nitric acid vapour.

Notwithstanding the presence of water in the charge, the first distillate is strong, becoming weaker as the distillation proceeds, until at the end it is almost pure water. The greatest evolution of nitrogen peroxide also occurs in the beginning, and as this is most soluble in strong nitric acid, it would contaminate the final product unless some means are taken to remove it. Its removal is, therefore, very important and is usually carried out in an absorption system.



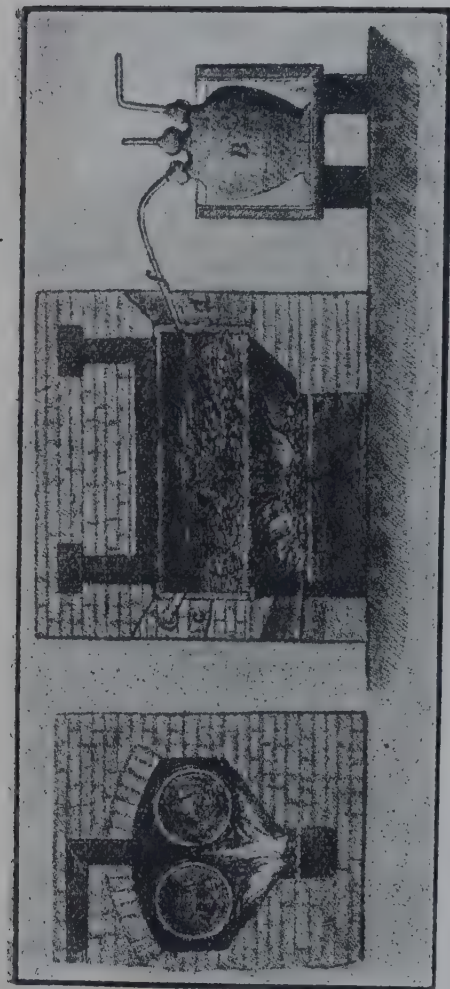


FIG. 13. NITRIC ACID PLANT.

A—Pair of cast-iron retorts in a furnace.

B—Stoneware condenser.

C—Movable door of flagstone to add the nitrate.

D—Movable door for removing sulphate.

E—Funnel through which acid is added.

F—Distilling pipe.

DISTILLING APPARATUS.

The distilling apparatus commonly used consists of a horizontal cast-iron cylinder or retort about 6 feet long four or five feet diameter, set in a furnace in such a way that the flame plays over its entire surface, heating all parts equally hot. Cast-iron is but little attacked by concentrated nitric acid or its vapours, and it is important that the retort be hot enough in all parts to prevent any condensation of acid. The charge of nitre is introduced through a door in the end, or side, of the retort, and the sulphuric acid is run in by a pipe. After the reaction the melted residue is run off by an outlet of the bottom of the retort and on cooling forms the so-called nitre-cake.

But all modern retorts are vertical pots suspended in brick setting. They are made of cast iron which is not attacked by nitric acid vapour as already stated or appreciably corroded by the sulphuric acid in the charge. These retorts are constructed in several sections to permit separate renewal according to the wear which they have suffered. The bottom piece is left unlined to permit free transmission of heat and hence the corrosion at this point, where there is always plenty of sulphuric acid, is very much less. The bottom of the pot is provided with an opening set in a trough for the removal of the residue at the end of the operation. The gas outlet and the charging hole are provided in the cover. These sections are luted together with acid-proof cement made up of asbestos powder containing a little finely powdered barium phosphate made into a thick paste with 5 per cent. silicate soda solution.

CONDENSERS.

In the older installations air condensation was relied upon, and this answers well in cold climates, but in

tropical countries like India it is better to employ condensers with water cooling devices, as in Guttman's apparatus and Hart's tube condenser, brief description of which are given later on.

PROCESS OF MANUFACTURE.

In manufacturing nitric acid the calculated amount of nitrate of soda is placed in a certain earthen vessel and then strong sulphuric acid is added by means of a funnel. The lid is replaced, and the vessel connected by means of a clay-lined tube with the glass tube dipping into the large stone-ware flask which serves the purpose of a receiver. The flask is connected by means of a tube to a similar vessel and that to a third vessel and so on, in order to completely condense the vapours which might have escaped through the first, second and third vessels. The retort on the earthen vessel is heated by means of the fire placed in the hearth, the smoke and hot gases being carried off by a specially constructed opening. At the outset of the operation the damper is so regulated as to shut off the lower channel, and cause the smoke and hot gases to pass through the bottom of the condensing vessels so as to prevent their cracking by the hot acid vapours. As soon as the distillation has fairly commenced, the damper is altered to shut off the passage just under the condensing vessels and allowed to escape through the other passage. The nitric acid condensed in the first receiver is sufficiently strong for immediate use, but to facilitate the condensation some more water is poured through the openings at the top of vessels into the other receivers, the acid from which is found to be weaker than the others.

RECHARGING.

After completing one charge and before putting another, the retorts are allowed to cool somewhat as the hottest part of the operation is at the end, which temperature would be too high for initiating a new charge. The soda charge is then dumped into the still, generally after drying if strong acid is required. The mantle plate is luted or charged on and the sulphuric acid is added rapidly. Evolution of nitric acid begins before all the sulphuric acid has been added, but a light fire is started before the evolution slackens and the heat is generally increased so as to ensure a steady flow of nitric acid from the retort into the receiving vessel.

BLEACHING NITRIC ACIDS.

The stronger acid prepared as described is usually yellow colour, due to the presence of hypo-nitric acid. If a colourless acid is desired, the crude acid must be subjected to a bleaching operation, conducted as follows:—The coloured acid is poured into large glass vessels placed in a water bath, heated to 80° — 90°C , and left in these vessels as long as any coloured vapours are given off. The escaping hyponitric acid is carried by means of glass or glazed earthenware tubes either into sulphuric acid chamber and there utilised, or into the flue of a chimney and thus into the air. Any hydrochloric acid present in the nitric acid is also carried off as chlorine. In order to remove any sulphuric acid it is necessary to distil the nitric acid over pure barium nitrate, while the last traces of hydro-chloric acid can be removed by distillation over silver nitrate.

RECENT METHODS OF DISTILLATION.

More recently improvements have been made in the manufacture of nitric acid, bearing especially upon the possibility of omitting the bleaching process, and a better mode of condensing the vapours of the acid.

Every practical chemist knows that the red vapour appears only at the outset and towards the end of the distillation of the nitric acid, and it is therefore only required to distil fractionally to obtain on the one hand a red coloured acid, and on the other a colourless acid. In order to practically effect the fractional distillation, a tap of porcelain or hard-fired stoneware is fixed in communication with the iron distilling vessel, while the tubes for delivery are connected with two different receivers. The tap is bored in such a manner, that at pleasure the communication can be adjusted with a particular receiver. By proper management therefore, it is possible to separate the red-coloured acid entirely and without any additional expense, from the colourless acid.

Very recently the distillation of nitric acid is conducted in a series of glass retorts placed on a sand-bath; there are generally two rows of retorts, the heating apparatus being a galley oven. If the acid is to be pure, the first condensations are collected in separate receivers, as the acid first condensed contains hydrochloric acid due to the chlorides contained in the nitrates under operation.

The proportion of materials employed is 30 parts of potassium nitrate to 29 parts of strong sulphuric acid, or,

17 parts of sodium nitrate to 14.5 parts of strong sulphuric acid.

The sodium bisulphate which remains may either be

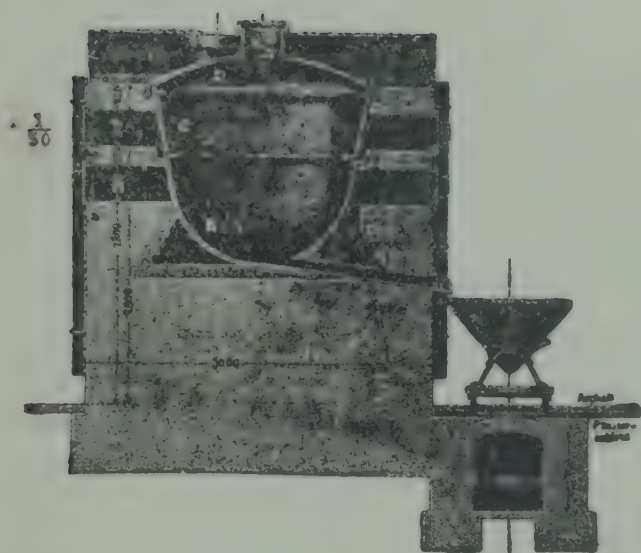


FIG. 14. NITRIC ACID PLANT. (ANOTHER).

A—An opening for removal of the residue after the operation.

B, C, D—Separate sections of the cast iron retort in a brick setting.

B is unlined.

B, B—Gas outlet and charging hole in the cover.



d for the preparation of fuming sulphuric acid, or may be mixed with common salt, and ignited, to produce perchloric acid and neutral sodium sulphate, available for the preparation of sodium carbonate.

The nitric acid resulting from the above operation is colourless, transparent fluid, having a sp. gr. 1.55 and boiling at 80°C .

A couple of processes are as follows:—

GUTTMANN'S APPARATUS.

In Guttman's apparatus the retort gases pass into a system of vertical earthenware pipes having very thin walls and joined at the top by bends, while they open at the bottom into a merely horizontal collecting pipe which is divided into sections by diaphragms. The sections are connected by U-tubes passing under the partitions. The diaphragms force the acid vapours to pass up one pipe and down the next, in order to go through the system. The thin walls of the vertical pipes allow efficient and rapid cooling by the cold water in the tank surrounding the pipes, and the vapours are quickly condensed. Air at 10°C is injected into the outlet pipe, where it converts some of the nitrous vapours into nitric acid, increasing the yield. The uncondensed nitrous vapours pass into the Liebig-Rohrmann plate tower, where they are absorbed by sulphuric acid or water.

HART'S TUBE CONDENSERS.

Hart's tube condenser for nitric acid is made of glass or earthenware tubes, and is placed above the brick arch supporting the retort, thus occupying but little floor space. The gas from the retort passes into a pot just at the side of the retort to condense some of the nitrous vapours and

thence through the vertical earthenware tube. This tube in its turn is connected with a number of glass tubes inclined slightly towards the earthenware tube and cooled by jets of water from the perforated pipe. From the glass tubes the uncondensed vapours pass to a plate tower. The acid condensed in the glass tubes flows back into the earthenware tube and then into the pot next to retort already mentioned, thus coming into contact with the hot vapours from the retort. This heats the acid so hot that the nitrous vapours are driven out and the light-coloured acid is run off into the receiver. In this apparatus the acid is condensed very quickly and little peroxide is formed. Frothing in the retort gives no trouble, as any overflow is caught and easily removed by special arrangement. The water dropping over the glass tubes can be so regulated that nearly all of it is evaporated on their surfaces giving great cooling effect with small consumption of water.

PURE ACID.

For preparing a chemically pure acid, pure materials are used, but it is best to distil the hydrated acid in glass vessels and receive the product which goes over separately as long as it occasions turbidity with a solution of silver nitrate. The receiver is then charged and the residue of the acid distilled off down to a small residue.

FUMING NITRIC ACID.

Fuming nitric acid is a solution of nitrogen peroxide in concentrated nitric acid. It is red in colour and has a specific gravity of 1.55 to 1.62. To prepare this, perfectly dry sodium nitrate and sulphuric acid (sp. gr. 1.84) are used. The nitrogen peroxide dissolves in the nitric acid to form the fuming acid. A little starch may be added

to assist in the reduction. An impure fuming acid is made by distilling a mixture of concentrated nitric and sulphuric acids.

OTHER PROCESSES.

There are two other competing processes of making nitric acid:—

- (1) By the direct union of oxygen and nitrogen of air by means of an electric arc.
- (2) By the oxidation of ammonia, synthetically manufactured.

Detailed description of the processes is beyond the scope of the present volume.

CHAPTER XVII.

ACETIC ACID.

ACETIC acid is more familiarly known under the name of vinegar, of which it is the important principle. It is obtained at a certain stage of fermentation of all sweet vegetable juices; but each of these imparts its own characteristics.

The pure acid forms a crystalline solid at any ordinary temperature but it combines with any quantity of water forming a very pungent, colourless liquid. The absolute acid is usually obtained by distilling the acetates of sodium or potassium with sulphuric acid, stirring a little peroxide of lead into the product, and then redistilling it. It can also be made by the direct oxidation of alcohol. The commercial acid is now principally made by the destructive distillation of wood, and hence it is generally known under the name of pyroligneous acid.

DISTILLATION OF WOOD.

The wood to be distilled is cut into pieces of a suitable length and thickness and is introduced into an iron retort placed over a furnace. From the upper part of the retort a pipe passes into the condensing chamber, where it is cooled by a stream of fresh water playing upon its outer surface, the condensed vapour pouring out into the receiver at the further end. The distillate, as it comes over, consists of a mixture of tar, acetic acid, methyl alcohol, acetone, naphtha, etc.

The liquor is distilled again in order to separate the acetic acid from other ingredients. To do this the crude good vinegar is placed in a vessel and boiled by means of a steam coil. The distillate passes in succession into two boilers each charged with milk of lime. Here the acetic acid combines with the lime forming calcium acetate while the methyl alcohol passing on, is condensed in a still leaving behind the tar in the retort.

PREPARATION OF CALCIUM ACETATE.

The contents of the boilers containing excess of lime and calcium acetate are run off and filtered. The solution is next evaporated with continual stirring in steam heated copper pans. The tarry matter rising to the surface is skimmed off. When the specific gravity reaches 1.116, it is run into copper pans. The tarry matter rising to the surface is removed and put over an iron plate to dry. The product contains about 80-82 per cent. of calcium acetate and 20 per cent. of water.

PREPARATION OF COMMERCIAL ACETIC ACID.

The acetate of lime is now distilled with sulphuric acid in a cast iron still provided with a scraping device inside to break up the solid mass which forms in the still and facilitate the escape of acetic acid vapour. The still is heated by direct fire and the acid vapour escaping from the retort is condensed by means of a copper condenser. Owing to the secondary reactions, some sulphuric acid is decomposed into sulphur dioxide, hence it is necessary to use some excess of the acid to convert the whole of the calcium acetate present in the retort.

The distillate contains about 75 per cent. of anhydrous acetic acid and a little sulphur dioxide. This acid

is then rectified in a large copper column still, heated by a steam coil. When starting distillation the air inside the apparatus is driven off and the temperature is gradually raised so as to allow the sulphur dioxide to pass off before the acetic acid begins to distil.

ACETIC FERMENTATION.

Acetic acid is also made by fermentation of alcoholic liquids with acetic ferment. Large wooden tubs are filled with shavings previously moistened with vinegar, upon which diluted (ten per cent.) alcoholic solutions are poured. The lower part of the tub, exposed in a warm room ($25-30^{\circ}$), is provided with a sieve-like bottom and all about it are holes permitting the entrance of air to the interior. The liquid collecting on the bottom is run through the same process two or three times, to ensure the conversion of all the alcohol into acetic acid.

GLACIAL ACETIC ACID.

Glacial acetic acid is nearly anhydrous containing 99 to 100 per cent. of pure acid, which crystallises on cooling to 16.5°C . To prepare this acid, the diluted acetic acid as manufactured above is neutralised with sodium carbonate. The sodium acetate formed is then used to expel its water of crystallisation. The anhydrous mass is next distilled with concentrated sulphuric acid. The distillate crystallises on cooling. On melting it forms a liquid of sharp odours known in commerce as glacial acetic acid.

ACETIC ACID FROM VINEGAR.

Acetic acid is also manufactured by distilling vinegar at a low temperature under reduced pressure. The small stills of tin capable of taking a charge of about 10 gallons

heated and pressure maintained at 15—20 inches
en through the outlet pipes, cooled by running water,
ps the acid. This distilate gives on an average 6 per
t. acetic acid. This is now precipitated as calcium
tate by adding lime, and the calcium acetate so
ained is distilled with a mineral acid when a 40%
tic acid is obtained.

Acetic acid is generally sold containing 33 per cent. of
l acid. Glacial acetic acid is preferred by some indus-
lists who dilute it to the required strength.

Absolute acetic acid is miscible in all proportions with
ter, alcohol and ether. It is a good solvent for essen-
oils, camphor, resins, etc. It has got extensive uses in
armacy and in dyeing. The use of acetic acid in the
m of vinegar for pickling is well known. It is also used
making toilet vinegar.

CHAPTER XVIII.

STEARIC ACID.

STEARIC acid very largely predominates as an article of commerce. It is employed in the manufacture of cosmetics, soaps, candles, face creams, rubber goods, etc. In the market it is available in three different grades namely as single, double and triple pressed stearic acid according to the proportion of oleic acid and palmitic acid contained in stearic acid. As will be shown, the product is purified by various degrees of pressure, which remove increasing amounts of the liquid oleic acid and broadly speaking, these grades represent the following composition:—

Grade.	Stearic acid. per cent.	Oleic acid per cent.
Single-pressed	85	15
Double-pressed	90	10
Triple-pressed	95	5

Stearic acid is a colourless, wax-like material, melting at 69.3°C having a specific gravity of 0.847 at this temperature. It belongs to the saturated series of fatty acids of the type indicated empirically by the formula $\text{C}_n \text{H}_{2n} \text{O}_2$, being the members having 18 carbon and 36 hydrogen atoms, as is probably best written $\text{CH}_3 (\text{CH}_2)_{16} \text{COOH}$. In the article of commerce actual stearic acid very largely predominates, but it follows from its natural occurrence that appreciable amounts of oleic and some palmitic acid are also present

proportions which vary somewhat according to the grade.

COMMERCIAL GRADES.

Stearic acid is also classified as either "saponified" or "distilled." These terms are derived from the processes involved in manufacture. These indicate differences which are of some importance to certain customers—as, for example, the manufacturers of candies, crayons and cosmetics. It will, however, be apparent to the chemist that not all stearic acid is saponified; and distillation, when employed, is a subsequent operation separate and distinct from saponification.

RAW MATERIALS.

High-grade tallows and the similar material and low grease stearin are the principal raw materials employed in the manufacture of the saponified grade. The natural colour of this product is a light amber, and since very particular users, such as crayon manufacturers and certain others prefer saponified acid on account of its harder texture and slightly lower contents of lactic acid, and have come to associate brownish colour with good quality, usually no attempt is made to decolorize this grade. Slaughter house grease, garbage grease, and similar materials of darker colour are the raw materials for the production of the distilled grade, these being rendered usable through the purification effected by the distillation process. It so happens that the cost of this process very nearly equals the savings effected through the utilisation of cheaper materials, and it is a matter of efficiency and economy of resources for the manufacturer to equip for the preparation of both grades. Distilled acid

is usually of somewhat lighter colour than saponified material of equal melting point and similar oleic acid content, but it is not naturally colourless, and the snow white products are obtained by resort to special decolorising methods.

WASHING THE GREASE.

The first operation is a washing, carried out in large wooden tanks equipped with open steam coils. Crude grease is run in dilute sulphuric acid, added, and the mixture is heated with live steam for approximately $1\frac{1}{2}$ hours. The principal purpose of this operation is the removal of mechanical impurities. Saponification of the grease is next accomplished by the use of any of the following methods'—

MILLY'S AUTOCLAVE PROCESS.

A combination of lime and hot water, known as Milly's "autoclave process" in which two to four per cent. of lime is made to do the work of saponification, for which 8.7 per cent. is theoretically needed, and for which 14 to 17 per cent. was at first used. The saponification is carried out in presence of water in strong closed metallic vessels, at a temperature of 172°C . One form of such vessel for the saponification by lime under pressure that has been much used is an egg-shaped cylinder. The lime soap after its separation is decomposed by sulphuric acid, four parts of acid to each three parts of lime used being taken. After complete subsidence of the calcium sulphate the free fatty acids are thoroughly washed with water and steam.

SULPHURIC ACID SAPONIFICATION.

The sulphuric acid saponification, followed by distillation, is almost exclusively followed in England. The

amount of sulphuric acid used has gradually been diminished, as it is found that a relatively smaller percentage will suffice. For offal fats some 12 per cent. is now used, for tallow 9 per cent., and for palm oil 6 per cent. The composition generally requires some hours at a temperature varying from 120° to 170°C . Milly modified this process by using a smaller quantity of sulphuric acid (to $3\frac{1}{2}$ per cent.), which he allows to act at a temperature of 150°C for 2 to 3 minutes only, and then boils with water. In this way the larger portion of the fatty acids are white enough to be for candle-making without previous distillation while some 20 per cent. only of them needs to be distilled. The form of apparatus for the distillation of the free fatty acids produced in the sulphuric acid saponification consists of a super heater, from which steam at 300°C is passed into the retort which is previously filled to three-fourths of its capacity with melted fat, which flows through the supply-pipes. The fatty acids distil out of the exit tube, are condensed by the worm and collected in a receiver.

SUPER-HEATED STEAM PROCESS.

The super-heated steam process of Wilson and Wynne is at present carried out in both England and Germany. In this process the fat, previously heated in a pre-heater vessel by the waste heat from the superheater below, flows into a retort. This retort must be kept at 290°C and 315°C and to this end is covered entirely above; the super-heated steam at 315°C comes into the retort by the top to the side, and some 24 to 36 hours is necessary to decompose and distil off a charge of fat. If the temperature falls below 310°C , the decomposition is extremely slow, while much above 315°C , acrolein forms from the decomposition of glycerine.

SAPONIFICATION WITH TWICHELL REAGENT.

The washed grease is run to steam tank, where saponification is carried out. The Twitchell reagent (sulphobenzene stearic acid) is added here and the stock boiled for 18 to 20 hours, at the end of which time the sweet water (glycerol) obtained as a by-product is run off.

A second boil now follows, and the crude fatty acid stock, free from glycerol, is again cooked in the tank employed for the original saponification. This treatment raises the fatty acid content to about 97 to 98 per cent.

DISTILLATION.

If the grade of grease employed is such as requires distillation in addition, the fatty acid mixture from the second boil is transferred to the distilling department, but if the saponified grade is being prepared, the charge is sent direct to the storage tanks in the cold process department. For distillation a typical fatty acid still is used, which is copper-lined and operated with super-heated steam under vacuum. The distillate is a highly refined fatty acid mixture, running a little less than 50 per cent. stearic acid and the residue in the still is the material known as stearin pitch.

COLD PRESSING.

The crude fatty acids obtained as above are heated to the melting point and run into dishes or troughs made of tin. These are placed in a room, the temperature of which is kept at 68° to 86°F (20° to 30°C), and left for 2 to 3 days to cool or solidify or until the contents have granulated. As the palmitic and stearic acids crystallise and form into cake, the dishes are emptied into canvas or woollen bags, which are carefully deposited between the

ces of a large upright hydraulic cold press, somewhat similar to that used in the rubber industry. Pressure is exerted, increasing in degree until the flow of the acid oleic acid ceases. The hard, thin cakes of crude stearic acid so obtained are known as single pressed stearic acid. This first pressing requires about $2\frac{1}{2}$ hours and produces a material of lower grade than any used in rubber compounding.

HOT PRESSINGS.

When further removal of oleic acid is required, this is accomplished by pressure under elevated temperature conditions. The cold-pressed acid is melted again, casted into pans and formed into cakes, which are wrapped in coarse cloth in preparation for hot-pressing. The melted acid for hot pressing is run into the tin dishes and set aside in a cooling room, temperature of which should be higher than before, or about 30°C . The blocks of stearic acid so obtained are ground to meal, filled in mats of hair or wool, and then submitted to a second pressing, in a horizontal hydraulic press, the plates of which can be heated. In this press, a pressure of six tons per square inch at temperatures of from 40° to 49°C is applied. The cakes so obtained are melted by steam, and a little wax being sometimes added to destroy the crystalline structure of the stearic acid.

Triple-pressed stearic acid is subjected to two hot pressings—the first for 3 to $3\frac{1}{2}$ minutes, and the second for 5 to 6 minutes with steam of 120 pounds pressure continuously circulating through the press. Double-pressed acid receives one hot pressing, which is of relatively long duration. Single-pressed acid of the standard rubber grade is also hot-pressed, and differs from the double in

that the period of hot pressing is shorter—namely minutes instead of 5. The time intervals mentioned above are the actual pressing periods and do not include the time consumed in loading and bringing up the press.

YIELD.

The yield of stearic acid obtained varies according to the fat used and the process of saponification employed. F. A. Sarg's Son (Vienne) use 3 per cent. of lime and a pressure of 10 atmospheres, and get 95 per cent. crude fatty acids and 30 per cent. of glycerine water (1 to 6° Be), and a final yield of 45 per cent. stearic acid, 5 per cent. of oleic acid and 5 to 6 per cent. of glycerine. In England, with the sulphuric acid and distillation process they get 60 to 70 or even 75 per cent. of fatty acids suitable for the manufacture of stearic acid.

DECOLORISATION.

Each grade is melted and boiled with sulphuric acid in a large tank in order to improve the colour. The product is drained while hot and is finally drawn off through pipes and again cascaded into pans which serve as moulds to form slabs of finished product.

Stearic acid is a colourless, wax-like material, melting at 69.3°C and having a specific gravity of 0.847 at this temperature.

STEARIN.

Stearin is the solid portion of fats insoluble in cold alcohol. There are three stearins or glyceryl stearates. It may be noted that stearin of commerce is the stearic acid.

Stearic acid has a definite function in rubber compounding. When added to brown plantation crepe rubber, or other sorts, for the purpose of enhancing the quality of the vulcanisation a less expensive and better product results through the presence in the stearic acid.

CHAPTER XL

OTHER ACIDS.

CITRIC ACID.

TO manufacture calcium citrate lemons are first cut in two and the pulp is scooped out by a suitable knife. The juice is then extracted from the pulp. On a small scale this can be done by a small screw press, very similar to one that is available for raw meat juice extraction, but on a large scale, larger and more efficient presses will have to be used.

The juice on leaving the mill is carefully distilled to obtain the oil, and afterwards while still hot, it is run into a wooden vat. Before running into the mixing vat, it would be an improvement if the hot juice were passed through filter bags. The vats are fitted with perforated steam coils in order to keep the juice hot and to act as agitators. They must be large enough to prevent loss from overflow by the foaming effervescence which takes place when chalk is added.

To prepare citrate of lime the hot juice in the vat is to be neutralised with chalk. The method of adding chalk is described below. A sufficient quantity of chalk is made into a cream with water and the mixture poured cautiously into the juice with constant stirring, slowly as the acid is neutralised. When the greater part of the chalk has been added, the mixture is well stirred and the effervescence is allowed to subside; a small quantity is then taken out and tested by the addition of a little of the

ture of chalk and water; if this produces an effervescence, more chalk must be added to the main quantity. Proceed cautiously and test at intervals, until no effervescence is produced.

It may be here noted that the liquor never becomes alkaline however long the boiling may be continued or ever great is the excess of whiting present; the adjustment of juice and whiting is therefore effected by ascertaining if the liquor effervesces with more whiting, or the precipitate effervesces with more juice. Pure citric acid is readily neutralised by whiting; malic and aconitic acid are not; the final acidity is thus possibly due to the presence of these acids. Citric acid, however, is not neutralised by chalk if phosphates, and specially ferric phosphates, be present. This fact will also explain the result. It is not advisable to neutralise completely by the use of whiting as vegetable impurities are then thrown down which afterwards difficult to separate.

After neutralisation, the citrate is allowed to subside, and the mother-liquor is run off through a tap fitted in the side of the vat. Hot water is then run in and steam is applied on to wash the citrate thoroughly. The washing should be repeated several times, the citrate being allowed to subside and the water run off between each washing. Finally it is agitated and run through a lower tap into the filter bags to drain. Afterwards it is placed in a press to extract as much moisture as possible; and then at once conveyed to the drier. The use of centrifugals is, however, more recommended for removing the water from citrate instead of the press. Citrate can conveniently be washed with a small quantity of hot water while in the centrifugals, and when the moisture has been removed by this means, it can be dried in a much shorter time.

When thoroughly dried, it should be placed in a room to cool before being tightly packed in barrels. It is important that the citrate should be thoroughly dried. If this is not done, much acid may be lost.

Citrate of lime when prepared by the method described above is a white powder and should contain about 64 per cent. of citric acid.

MANUFACTURE OF CITRIC ACID.

The starting point in manufacturing citric acid is calcium citrate or commonly known as citrate of lime.

The precipitated calcium citrate is washed with water on a filter. It is next brought by the addition of water to the state of thin cream and decomposed, with constant agitation, by the addition of a small excess of sulphuric acid. The occurrence of an excess of sulphuric acid is known by the liquor affording a precipitate with a strong solution of calcium chloride after some minutes standing.

The citric acid liquor is then separated from gypsum which is washed on a filter. The liquor is evaporated in shallow leaden baths by steam heat. Much gypsum is at first deposited; from this the clear liquor is run off and further concentrated. When strong enough to crystallise, the hot liquor is run into a wooden tub provided with an agitator, and the liquor is run into a wooden tub provided with an agitator, and the liquor is kept in constant motion while cooling; by this process known as granulation, the citric acid is obtained as a crystalline powder. The mother liquor is again concentrated, and acid is again obtained by granulation. The process may be repeated a third time. The liquor is then too dark and impure for further crystallisation, and is known as "old liquor." The

culated citric acid when drained, and if necessary, freshly washed, is redissolved, decolourised by heating with animal charcoal (previously freed from phosphates with hydrochloric acid), again concentrated to the crystallising point, and poured into leaden trays about 3 inches deep; the crystals here formed are the citric acid of commerce.

The juice contains about 400 to 425 grammes of citric acid to the litre. 100 litres of raw juice yield before 8 kilogrammes of calcium citrate. The latter consists of 64% of citric acid to 36% of calcium oxide. 100 kilogrammes corresponding to 800 litres, of concentrated juice yield 1200 kilogrammes of moist calcium citrate with 60% of water, i.e., corresponding to 450 kilogrammes of dry salt, which contains about 5% of impurities and yields 320 kilogrammes of citric acid.

CALCIUM CITRATE (IMPROVED PROCESS).

The concentrated lemon juice is diluted to 50° Be and heated up to 80°C by means of a direct-steam current, in wooden barrels provided with stirring appliances.

Out of a higher placed basin, wash lime of specific gravity 3°—5° Be, heated to boiling point, is allowed to fall into the solution of citric acid, in the form of a thin jet. The addition of wash-lime is continued until about three-quarters of the acid is neutralised, the rest being precipitated by means of finely ground calcium carbonate. Under the barrel (in which the citrate is precipitated) is placed a filter-box with a wood sieve, on which is stretched a piece of jute-cloth; the box is provided with an exhaust opening. The contents of the barrel are allowed to flow into the filter-box and the brown liquid

filters through. If the process of precipitation has been correctly conducted, the precipitated calcium citrate will be roughly crystalline and heavy like rough sand. If, on the other hand, it is voluminous and slimy the process was incorrectly carried out; the liquids were either not enough or they were too concentrated.

The calcium citrate left behind on the filter is now washed with boiling water until the liquid that flows off is as clear as water. For this purpose a spacious wooden vessel is employed, in which the water needed for washing the citrate heated to boiling-point by direct steam current and then allowed to flow into the filter box.

TARTARIC ACID.

Tartaric acid occurs in nature either in the free state or in combination with potassium and calcium as tartrate in many vegetable juices such as tamarinds, mulberries, pineapples unripe beet root and more particularly in grape juice in combination as potassium bitartrate. A considerable industry is carried on in wine-producing countries in the production of tartaric acid from the less containing potassium bitartrate and calcium tartrate.

One of the most important uses to which the acid is put is in certain photographic processes for printing and developing. It is also used for medical purposes and in the preparation of baking powder effervescent drinks, Seidlitz powders, etc. It is used by the calico printers to liberate chlorine from bleaching powder and in the production of a number of dyestuffs, as a resist for aluminium and other mordants and in the discharge colours for Turkey red. It is also used in the mordant bath in dyeing wool; for brightening the colour of silk after dyeing; and for tendering cotton fabrics.

MANUFACTURING PROCESS.

The starting point in the preparation of tartaric acid "argol" which is a crystalline crust after fermentation of the grape juice. The lees after the fermentation of grape juice is another source of tartaric acid.

ACID FROM ARGOL.

When argol is made the source of tartaric acid, the usual practice is to powder the crystalline argol and mix it with water. Hydrochloric acid is then added to dissolve the argol and the whole mass is boiled. As a general rule, 500 kilos of argol will require about 4 to 5 cubic meters of water and 110-120 kilos of crude hydrochloric acid of 20° - 22° Be. The solution is then nearly neutralised with milk of lime which causes the deposition of calcium tartrate leaving potassium tartrate and calcium chloride in solution. Care should be taken not to add sufficient milk of lime to neutralise the solution. The small amount of potassium hydrogen tartrate left in the solution is decomposed with pure precipitated calcium carbonate. The addition of the calcium carbonate should be so regulated that the solution still remains slightly acid. The whole is then allowed to cool to about 40°C , the liquid is filtered off with the aid of a suction pump and the residue washed with water. The calcium tartrate is then mixed with water and decomposed with dilute sulphuric acid, a portion of the solution is tested at intervals to ascertain when sufficient acid has been added. For this purpose use calcium chloride as a re-agent, as this does not give any precipitate with calcium sulphate contained in the solution but precipitates the free acid.

The gypsum resulting from the decomposition is washed on a vacuum filter and the liquor is evaporated

in steam-heated leaden pans, or in vacuum pans. After partial concentration the liquor is run off from the gypsum which has deposited on the sides of the pan, and is concentrated to the crystallising point. It is then run into a tub and continuously agitated by mechanical stirrer to produce a granular salt. This system of crystallisation separates the salt in about a fifth of the time required for crystallisation by standing. The mother liquor from the salt is concentrated and a second and a third crop of crystals are obtained by granulation as above; the residual dark coloured impure solution is known as "old liquor." The granular salt is redissolved, heated with animal charcoal which has been freed from calcium phosphate by digestion with hydrochloric acid; the solution is filtered, concentrated and crystallised in cylindrical leaden pans about 2 feet deep. Tartaric acid thus prepared is not free from lead. It may be noted here that crystallisation is assisted by the addition of sulphuric acid, in which case the acid is less soluble than in water.

The "old liquor" as mentioned above is then diluted and precipitated with milk of lime. This produces a further quantity of calcium tartrate which is worked up as described before. It is however found that as the impurities accumulate in the liquors, it is more and more difficult to bring about crystallisation so that continuously more and more acid will be required for crystallisation.

ACID FROM LEES.

When the wine less or low argols are used as source for tartaric acid, the less or argols are first dried and crushed, stirred in a tank with water and heated by steam for half an hour and then transferred to the pressure boiler. The less are then treated with the requisite quan-

of hydrochloric and (21-22°C), filtered, pressed and dried. The tartaric acid is precipitated with lime and sodium carbonate and the remaining operations are the same as in the treatment of argols with the exception that there is no need to add calcium chloride or sulphate.

ACID FROM GREEN TAMARINDS.

Green tamarinds received in bulk are given a preliminary washing to remove dirt, etc. and subsequently dried in a suitable equipment to produce a homogeneous mass. The mass is then treated with toluene, ether, carbon tetrachloride, sulphur dioxide, chlorine, etc. When whole fruits are employed, a greater time would be necessary for the chemicals to act on the tissues. When the reagents have acted effectively, drops of moisture could be seen on the surface. This reaction of plant tissues to the chemicals is correlated with both the time of exposure and the quantity of the reagents. The inorganic acids bring about plasmolysis even under low concentrations, the same being completed in about 6 hours which could also be reduced under certain conditions. At the end of this period, the tissues are less turgid and part with a portion of the water initially present more readily than before. The entire mass is therefore treated in a hydro-extractor to remove as much of the juice as possible, the resulting solid being dried either in the sun or at about 50°C under artificial heating. Generally, drying is complete in about 36-40 hours, so that the dried mass is conveniently stored. The utilisation of the solid for extraction of the residual acid could be carried out subsequently. For this purpose, the material is either leached in open vessels or preferably in closed vessels. In this case extraction with steam is not quite essential. The prevailing

temperature would suffice, since the acid is highly soluble even in cold water. The resulting leachate or extract is still rich in tartaric acid.

TREATMENT OF AQUEOUS EXTRACTS.

The extract secured either by centrifuging the pulp from molysed fresh material or by leaching out the residue from the dried solid, contains among other water soluble components, albuminoids which interfere with the precipitation and purity of the lime tartrate, besides mechanical impurities derived from the fruit itself in the form of thin pulp. The extract is next boiled for a short interval to precipitate the solids. This is then filtered. The filtrate contains chiefly tartaric acid.

LIME TARTRATE FROM EXTRACTS.

The clarified extracts obtained in the above manner contain tartaric acids varying between 2.5 and 3.0 per cent. For several reasons it does not appear worth while to concentrate this extract. It is advantageous to precipitate the acid from this extract. It is advantageous to precipitate the acid as its lime salt through the addition of lime or chalk. In the latter case however, the tartaric acid content in the extract must first be determined preferably as the insoluble cream of tartar, so as to ascertain the amount of lime or chalk to be added to the stuff. Having calculated the exact amount of lime to be mixed, the clarified extract is treated with the required quantity of lime in the form of milk of lime or with the reckoned amount of chalk, so as to neutralise the acid. It is of the greatest importance that the chalk or lime employed must be highly pure, otherwise the impurities of iron or magnesium would contaminate the final product. The neutralisation of the tartaric acid in the extract is

important item and requires careful control. When the neutralisation is complete as indicated by litmus, the extract becomes generally turbid and affects the purity of the lime tartrate. It is therefore necessary to neutralise the extract till it reacts weakly acidic. The quantity of lime added will thus be less than what is quantitatively required for neutralisation. In this case, the extract is clear. Another advantage secured by keeping the reaction acidic in the precipitation of the lime tartrate relates to the fact that the latter which is usually granular though in a fine state of division, does not cake on drying. Where the neutralisation is thorough and complete as determined by litmus, the impurities precipitate with the lime tartrate and in cake formation, when drying. The granular precipitate obtained in this manner is easily filtered in a filter-press, following a preliminary decantation if necessary. The precipitate is then washed with cold water and dried.

TARTARIC ACID FROM CALCIUM TARTRATE.

The lime tartrate is next transferred to a lead-lined wooden vat provided with a stirring arrangement consisting of wooden paddles and with inlet for steam and composed with the required quantity of sulphuric acid. In practice, the following procedure is adopted. A quantity of water or preferably medium liquor from a previous batch of the decomposed tartrate, is introduced into the vat and mixed with a quantity of sulphuric acid equivalent to the amount of lime or chalk employed for neutralising the tartaric acid. Steam is then led into the vat to maintain the liquid at a higher temperature. It is imperative that for effectively decomposing the tartrate, this should be in the neighbourhood of 70°C . Sulphuric acid is generally employed in the form of oil of vitriol (sp. gr. 1.640).

FILTRATION OF CALCIUM SULPHATE.

The filtration of tartaric acid liquid from the decomposed lime tartrate is carried out in a filter press, made of wood, the filter cloth being hessian or jute. The calcium sulphate settles on the filter cloth and forms a thick filtering medium, the filtered liquid being drawn off at the bottom.

TREATMENT OF THE ACID LIQUORS.

The strong liquor containing tartaric and sulphuric acids is transferred to the evaporators for being concentrated. The volume resulting from such concentration is generally half the initial one and the liquid would approximate to a sp. gr. of 1.390. The temperature at which this concentration is effected should not be higher than 80°C , since overheating leads to charring of the acid. When this concentration is effected in the open the agitators are made of wood, and the other component parts are either lead-lined or are made of wood.

The strong fresh liquor is concentrated to a sp. gr. of 1.390 when it generally yields a crop of crystals, and the mother liquor is concentrated again, this process being repeated four times.

This crystallisation is effected in lead-lined vessels provided with cooling coils. After the liquid is cooled, the crystals are separated in a hydro-extractor. The brown crystals obtained are next washed in the extractor with water.

PURIFICATION.

The crystals obtained above are somewhat brownish due to the presence of sulphuric acid, calcium sulphate and contaminated colouring matter. The purification of

these crystals, can be effected by means of animal charcoal. The amount of charcoal required will vary with the intensity of the colour but roughly corresponds to 0.5 per cent. in the weight of the solid employed. Besides this a small amount of barium sulphide is to be added to remove the sulphuric acid. After these treatments the density of the solution must not be less than 1.30. The liquid is filtered and concentrated to the crystallisation point in enamelled iron vessels. On settling and after cooling the bright crystals are formed and removed in a hydro-extractor. Finally the crystals are to be dried in a chamber at about 100°F.

PHOSPHORIC ACID.

There are three distinct acids usually grouped under this head, namely, Metaphosphoric Acid, Pyrophosphoric Acid and Orthophosphoric Acid.

METAPHOSPHORIC ACID.

To manufacture metaphosphoric acid bones (calcined to whiteness and powdered), 3 parts, are digested for several days in sulphuric acid, 2 parts, previously diluted with water, 6 parts, the mixture being frequently stirred during the time; a large quantity of water is next added, the whole thrown upon a strainer, and the residual matter washed with some hot water; the mixed liquors are then precipitated with a solution of carbonate of ammonium, in slight excess, filtered from the insoluble and finally ignited in a platinum crucible.

Metaphosphoric acid is also prepared by acting upon the anhydride with cold water. When phosphoric acid is added to a strong solution of phosphate of sodium, and the mixture, after concentration, is exposed to a low temper-

ature, prismatic crystals are deposited. These after being strongly heated to expel their basic water, are pure metaphosphate of sodium. From the solution of this salt in cold water, a solution of pure metaphosphoric acid may be obtained, as above, by means of nitrate or acetate of lead and sulphuretted hydrogen.

Metaphosphoric acid precipitates the salts of silver white, and is distinguished from the other modifications of phosphoric acid by the property which its solution possesses of coagulating albumen.

PYROPHOSPHORIC ACID.

Pyrophosphoric acid may be prepared by strongly heating common phosphate of sodium. The water of crystallisation only is at first expelled, and the salt becomes anhydrous; but as the temperature reaches that of redness the salt loses water and is decomposed. By solution of the altered salt in water, crystals of pyrophosphate of sodium may be obtained. A solution of this last compound, treated with nitrate of lead, and the resulting precipitate, suspended in cold water, and decomposed by sulphuretted hydrogen, yields a solution of pure pyrophosphoric acid.

ORTHOPHOSPHORIC ACID.

Orthophosphoric acid, is prepared technically by digesting bone-ash with diluted sulphuric acid for several hours. The calcium sulphate is filtered off, and the phosphoric acid evaporated to a specific gravity of 1.7. The product is impure, containing acid calcium phosphate. Phosphoric acid is also made by the electric furnace process. A mixture of calcium phosphate, sand and coke is fed by a worm-conveyor into a closed electric furnace, provided with an outlet above for the gases and phos-

phosphorus vapour, a slag hole and carbon electrodes between which an electric arc is struck. The phosphate is decomposed at a high temperature by silica when calcium silicate and phosphorus pentoxide vapour are formed. The silicate forms the molten slag and vapour of pentoxide is reduced by the carbon at about 1500°C , forming carbon monoxide and phosphorus vapour. About 5 kilowatt hours are used per kilogram of phosphorus. Air is admitted into the chamber to burn the phosphorus vapour to P_2O_5 , and CO , to CO_2 ; water is sprayed into the cooled mass and crude 85 per cent. phosphoric acid is separated by subjecting the fumes to high tension discharge such as is given off from a point or fine wire attached to a pole of an electric machine or induction coil. The acid may then be purified. Blast furnaces are also used in the process.

Pure orthophosphoric acid is obtained by the oxidation of phosphorus with nitric acid. Oxides of nitrogen are evolved.

TANNIC ACID.

Tannic acid is a powerful astringent principle from certain tannin-bearing materials like galls, myrobalans, dividivi, sumach, catechu, etc. The acid is extensively used in the leather industry. In its pure form it is used as an astringent in medicine. It is lately being used in the preparation of inks.

Tannic acid is found to the largest extent in galls. Aleppo galls contain 50-60 per cent. of tannic acid whereas Chinese galls yield as much as 70 per cent. In moderate amount it occurs also in sumach, dividivi, myrobalans, etc.

METHOD OF MANUFACTURE.

The principle involved in the manufacture of tannic acid is one of percolation. The gallnuts which are chiefly employed as the raw ingredients are made into moderate fine powder. The mass is then introduced into a percolator which is a cylindrical vessel open at both ends. The upper opening is fitted with an air-tight stopper and the lower end adjusted to the neck of a receiver. The upper vessel, or percolator, is about half filled with coarse powdered galls, which are prevented from falling through the lower opening by a plug of cotton, and the powder is then covered, in successive portions, with ether, which has been previously shaken up with a little water. The stopper is now inserted in the mouth of the percolator, and the mixture allowed to digest for several hours, after which the stopper is withdrawn, and the liquid allowed to filter into the receiver beneath. When all the liquid has passed through, the powdered galls are washed with more ether introduced at the top as before. After standing for a short time, the filtered liquor will be found to separate into two distinct strata of unequal density. The tannic acid and gallic acid, being both extracted by the mixture of ether and water, now separate; the lower stratum being a solution of tannin (generally of an amber colour) in water, and the upper stratum an ethereal solution of other substances contained in the galls, the most important of which is gallic acid.

The two solutions are next separated; the aqueous solution of tannin is gently evaporated to dryness and finally exposed to an oven heat, at a temperature not exceeding 212° Fahr. The result is an amorphous, or uncrystallised mass of tannin, nearly if not quite pure, the yield being frequently about 40 to 45 per cent. of the

weight of galls used. The ether in the lighter liquid is recovered by distillation, over a water bath, with the aid of a Liebig's condenser, supplied with ice-cold water.

A SECOND METHOD.

First reduce the wood or bark by cleaving, breaking, sawing, etc., to small pieces about $\frac{1}{2}$ inch thick. These pieces are placed in closed vessels of copper or enamelled iron, and treated with water at about 20° to 75°C . (68° to 167°F .), under pressure, so as to extract tannic acid, etc., the different vessels forming a "continuous working battery," and being connected with each other by pipes, which may be heated, if desired. If, for instance, the "battery" consists of twelve vessels, pure water, under pressure, is allowed to enter the first vessel, where the process begins, and is continued until the densities of the liquids inside and outside the bark-cells are equalised. The liquid is afterwards allowed to pass from the first into the second vessel, where the tannic acid solution will become more concentrated. From the second vessel the liquid passes into the third, and so on up to the eleventh vessel, where the concentration of the liquid is almost equal to that in the cells containing the raw materials. During that time, pure water has been supplied to the first vessel, by which its contents become exhausted and may be discharged. Pure water is now admitted to the second vessel, and the twelfth filled with raw material. The extracted liquid is afterwards made to pass into the twelfth vessel the first filled with raw material, the second discharged and pure water allowed to flow into the third vessel, and so on, in such a manner that the contents of ten vessels are continuously subjected to dialysis. The necessary temperature of the water may be maintained by pro-

viding the connecting pipes with heaters of any suitable construction. The extract obtained by this process may be further concentrated in vacuum pans, or may be employed directly for the manufacture of leather.

A THIRD METHOD.

A third method of making tannic acid on a commercial scale from gallnuts follows: The finely powdered material is stirred with sufficient water at 50° – 60°C to form a concentrated aqueous extract, and after filtration the clear liquid is agitated with one-fourth of its volume of ether until an emulsion results. After standing for several days, the upper ethereal liquid which has separated is removed, and the layer, which contains all the tannin matter, is run into a still and the ether which is present is recovered. After cooling the syrupy liquid is spread out on sheets of tin, and heated by means of a steam coil, when the gallo-tannic rapidly puffs up and dries.

PURIFICATION.

Thus prepared the commercial tannic acid contains some quantity of gallic acid and other impurities. To remove these the material may be washed with ether or the aqueous liquid fractionally precipitated with common salt, the precipitate dissolved in ethyl acetate and the tannin recovered by evaporation under reduced pressure.

PROPERTIES.

Pure tannic acid is nearly colourless, inodorous, pre-eminently astringent in taste, uncrystallisable, very soluble in water, and less soluble in pure alcohol and ether. It combines energetically with gelatine.

By exposure to the air, a solution of tannic acid gradually becomes turbid, and deposits a grey crystalline

powder, which is gallic acid. By contact with the air oxygen is absorbed, and an equal volume of carbonic acid evolved; only a portion of the tannic acid, however, is decomposed, and is converted into gallic acid.

GALLIC ACID.

A quantity of nutgalls are reduced to powder, and this next made into a paste with water; in this state, the mass exposed to the action of the air, in a warm situation the temperature being from 70° to 80° Fahr., for two or three months, more water being added from time to time, to make up for that which is lost by evaporation. At the end of the above period, the mouldy, dark-coloured mass is strongly pressed in a cloth, and the solid portion boiled in a considerable quantity of water. The solution is to be filtered whilst hot, and on cooling, crystals of gallic acid will deposit at the bottom of the vessel. These crystals are afterwards to be well drained, and pressed between folds of white blotting paper. They are next to be purified, by boiling them with about one-sixth of their weight of prepared animal charcoal in eight parts of water. The solution is to be again filtered whilst hot, and the clear liquor set aside to cool, when pure crystals of gallic acid will be obtained, which must be well drained and dried over a water-bath.

Pure gallic acid assumes the form of white or nearly colourless feathery crystals of a beautiful silky lustre; the commercial acid, however, is usually of a pale yellow colour; it is soluble in alcohol, and also, sparingly, in ether; its solution in water undergoes decomposition when exposed to the air. On being strongly heated gallic acid is converted into meta-gallic acid.

The principal use of pure gallic acid is in the photography. It is also largely used in the manufacture of stylographic inks. It is employed in medicine.

PYROGALLIC ACID.

When gallic acid is subjected to dry distillation, at a temperature between 110° and 120° Fahr., a white crystalline substance distils over, which is pyrogalllic acid. Its preparation is as follows:—Finely, powdered gallic acid is treated with successive portions of cold water till exhausted, and the infusions carefully evaporated to dryness, when they leave a spongy, deliquescent mass, which is to be pulverised and spread equally over the bottom of a cast-iron pan, 3 or 4 inches deep, and about a foot in diameter. The top of the pan is covered with a diaphragm of bibulous paper (filtering paper) pasted round its edges, pierced with pin holes, and surmounted by a paper chimney 12 to 18 inches high. The pan is then cautiously heated for 10 or 12 hours, over an oil-bath, so as to preserve a temperature as nearly as possible at about 400° Fahr. White crystals of sublimed pyrogalllic acid collect in the cap, the other products are chiefly absorbed and retained on the paper diaphragm.

Pyrogalllic acid is white, crystalline without odour, and of a bitter taste. When pure it does not red colour litmus paper, it is very soluble in water, ether and alcohol. This acid is much used in photography.

CARBONIC ACID.

Carbonic acid is formed when carbon dioxide is dissolved in water. Though an unstable body, carbonic acid forms with bases a great series of well-known compounds known as carbonates. Carbonic acid is employed

commercially for impregnating water under pressure (making what is called soda water), as a fire extinguisher, and for refrigeration.

In preparing carbonic acid, the first step is the preparation of carbon dioxide, which by itself is a colourless gaseous product. It is produced whenever carbonaceous bodies are burned with a sufficiency of oxygen. It can readily be produced by the action of acids upon carbonates, such as calcium carbonate (chalk and marble) and when hydrochloric acid is used in the process, there is almost an immediate evolution of carbon dioxide with a brisk effervescence, calcium chloride being left behind in solution. Sulphuric acid should not be used in place of hydrochloric acid, for though the action is almost as rapid it is short-lived and stops after a short time due to the deposition of insoluble calcium sulphate on the mass. The gas is passed through water which dissolves it.

It is observed that one volume of water at 0°C dissolves 1.713 volumes of the gas (or 19.75 lbs. per 1000 gallons of water).

SALICYLIC ACID.

For the preparation of salicylic acid sodium phenate is combined with carbon dioxide, forming sodium phenyl carbonate, which, on heating is converted into sodium salicylate. The operation comprises:—

(2) Carbonation and conversion to sodium salicylate.

(3) The separation and purification of salicylic acid.

It is essential that the sodium phenate should be finely powdered and that it should be absolutely free from moisture. When hot, it readily oxidises in the presence of air, so it is advisable to conduct the operation of drying

and powdering in a shallow vacuum pan fitted with powerful stirring gear. In order to obviate the risk of the dried phenate absorbing moisture when handled, it is desirable to carry out the drying and powdering in a vessel so constructed that the dried product can be transferred, without exposure, to the vessel in which the carbonation is to be conducted. The most suitable type of plant for the latter purpose is a horizontal jacketed shell autoclave, provided with powerful rotating stirrers which scrape the sides. An inlet pipe for the introduction of the carbon dioxide is required; also an outlet to a condenser and receiver (provided with a side glass) which is connected with a vacuum pump, so that the phenate may be submitted to a final drying before carbonation commences. Either cold water or steam at 60 lbs. pressure can be circulated through the jacket.

Phenate is made by dissolving phenol in 40% caustic soda solution. The mixture is then introduced into the vacuum pan, in which it is evaporated to dryness *in vacuo*, the stirrers being kept continuously in motion. Heating, to a temperature of 120° – 130°C , is continued for about an hour after the condensation of water has ceased. The sodium phenate is now in the form of a fine powder and is transferred while still hot to the autoclave. The latter is rendered vacuum and the stirrer started. The vacuum valve is then closed and dry carbon dioxide is introduced. Absorption takes place rapidly, with rise of temperature. The gas is passed in until the gauge shows a positive pressure of 3 atmospheres. Steam is then turned on and the temperature raised to 120° – 130°C , more gas being introduced to maintain the pressure. Heating is continued for 3 hours after absorption is complete, after which time it is stopped and the

cold water circulated again, to reduce the temperature somewhat. The excess of carbon dioxide is used in the carbonation of a charge in another autoclave. Water is added and the solution of sodium salicylate pumped out, filtered and transferred to wooden vat with stirrer. The salicylic acid is precipitated by addition of acid, centrifuged off and dried. The impure acid is purified by distillation, either with superheated steam or with air. In the latter case the acid is heated in a shallow still provided with a stirrer, or in a shallow tray, to a temperature of about 140° — 150°C . A current of air, preheated to the same degree, is blown through and over the stirred mass and thence into a suitable condensing chamber, in which provision is made for removing the heat, also for filtering out the last portion of salicylic acid flakes from the air.

Salicylic acid is both antiseptic and antipyretic. It is a constituent of dusting powders and, dissolved in collodion, is employed as solvent for corns and warts.

OXALIC ACID.

Oxalic acid is produced in numerous reactions, more especially in the oxidation of organic matters. The action of nitric acid on alcohol, sugar, glycol, starch, and on cellulose yields oxalic acid. In the same way fused potash acting on sugar, starch, pectic acid and on wood sawdust produces oxalic acid. It is this latter reaction that is utilised commercially to produce oxalic acid very cheaply. The wood sawdust for, this purpose is first brought to the state of paste by mixing it with an alkaline solution marking 37° to 38°Be (69° to 72°Tw.), sp. gr. 1.345 to 1.360, consisting of potash and soda in the proportion of one equivalent of the former to two equivalents of the latter. When it is desired to make oxalate of potash, then

caustic potash alone is of course used. To 100 lbs. of saw dust, 300 to 350 lbs. of caustic potash are added in solution. The paste thus obtained is then carbonised by heating it in a horizontal cylindrical retort, slightly inclined, capable of revolving on its axis. This retort being heated to dull redness, the mixture swells up during the process of the evaporation, with generation of gases, which are burnt in the furnace. The motion of the retort conveys the carbonised material from the upper to the lower end of the retort whence it is taken to lixiviation tanks.

For this purpose the charred mass is dissolved in minimum quantity of water at 10° to 20°C ; this dissolves the alkaline oxalates, which are more soluble in cold than in hot water. The liquid, after settling, is decanted and evaporated to dryness. The oxalates are again dissolved in cold water, the solution being brought to the boil and treated with lime to precipitate oxalic acid, and regenerate the caustic alkalis which remain in the liquid and can be utilised for a subsequent operation. The precipitate of oxalate of lime is washed with water, then decomposed by a slight excess of sulphuric acid in order to liberate oxalic acid. One molecule of oxalic acid requires three molecules of sulphuric acid. The salt is rubbed up with water to a thin paste, and the requisite amount of sulphuric acid at 15° to 20°C is added with stirring. After adding water it is heated for a few hours, then filtered to separate the sulphate of lime. The solution of oxalic acid, after evaporation, is left to crystallise in lead vessels; but, as the crystals of oxalic acid so obtained are slightly coloured, they are purified by redissolving them in water and recrystallising. The residue, left after exhausting the carbonised mass with cold water, is calcined in a reverberatory furnace; yielding a mixture of carbonate of

potash and soda, which is causticised with lime for use in subsequent operation. From 100 lbs. of wood sawdust 10 to 60 lbs. of oxalic acid are obtained.

Oxalic acid is used in very large quantities in calico printing and manufacture of blue ink.

CHAPTER XX.

AMMONIA AND AMMONIUM COMPOUNDS.

AMMONIA.

ON a small scale ammonia is made by heating ammonium chloride with calcium oxide or lime, after being carefully dried and heated together. The evolving gas is dissolved in water.

Ammonia and salts of ammonia are largely obtained from ammoniacal liquor of gasworks. The crude coal gas obtained by the distillation of coal contains a number of impurities—tar, ammonia, sulphuretted hydrogen, organic sulphur compounds, naphthalene and cyanogen. Elaborate arrangements are made by the producers of illuminating gas to separate these gases and collect them for future use before the coal gas is ready for distribution to the public. Ammoniacal liquor is an important by-product in making coal gas and this is at present the fruitful source of ammonia.

COMMERCIAL AMMONIA.

To prepare ammonia from ammoniacal liquors the usual practice is to treat the gas liquor with lime. The whole is then distilled, when ammonia is driven over and condensed in water.

The details of the process follow:—In gas works the gas liquor as drawn from the condenser is allowed to settle. The settled gas liquor is made to pass through a cylindrical chamber containing a series of narrow tubes heated by steam and also by the waste gases passing

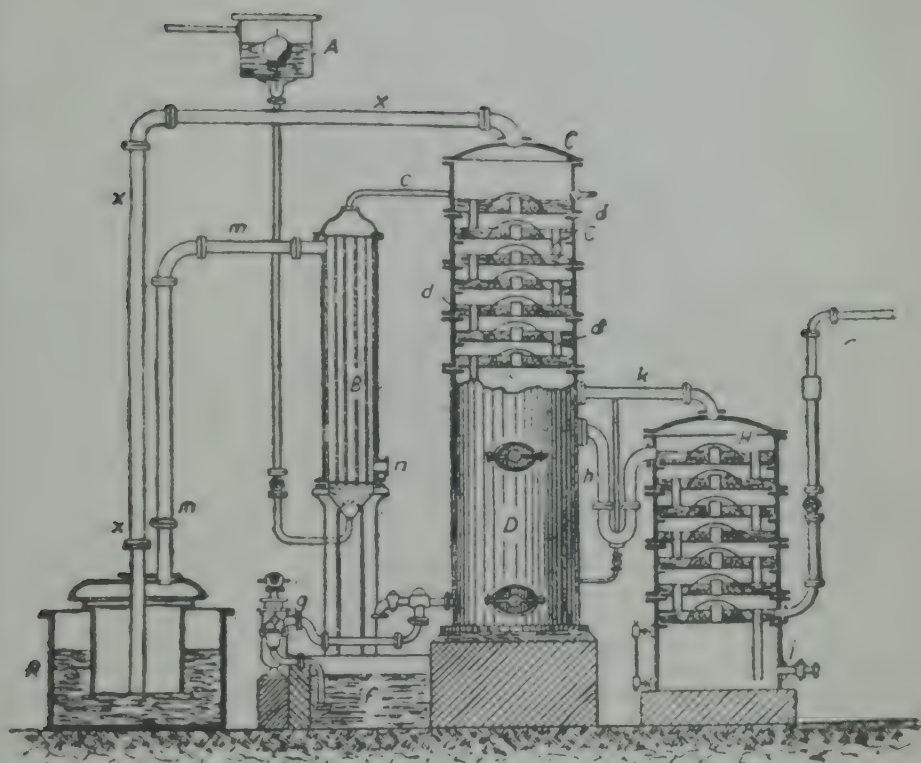


FIG. 15. AMMONIA STILL.

A—Regulating Tank.

B—Pre-heater.

C, H—Column.

d—Overflow pipe of the compartments of C.

D—Still.

g—Pump.

h—Connecting tube.

f—Lime Tank.

i—Passage for ammonia-free liquor.

R—Saturator.

m m—Steam pipe.

X X—Pipes conveying ammonia.



1. The first part of the drawing shows a plan view of the building, with the central tower and the surrounding structures. The plan view is drawn in a simple, schematic style, with lines indicating the walls and the internal divisions of the building. The central tower is the most prominent feature, and its plan shows a series of rectangular sections. To the left of the tower is a smaller, rounded structure, and to the right is another structure with a gabled roof. The plan view is drawn in a way that shows the overall layout of the building and the relative positions of the different parts.

2. The second part of the drawing shows a section view of the building, with the central tower and the surrounding structures. The section view is drawn in a simple, schematic style, with lines indicating the walls and the internal divisions of the building. The central tower is the most prominent feature, and its section shows a series of rectangular sections. To the left of the tower is a smaller, rounded structure, and to the right is another structure with a gabled roof. The section view is drawn in a way that shows the internal structure of the building and the relative positions of the different parts.

through this chamber. The heated liquor is then forced to the top of a tall tower where it meets an upward current of steam from a boiler which causes the volatile ammonium compounds such as the carbonate, sulphide and cyanogen to be liberated. The non-volatile or fixed compounds such as the chloride and sulphate flow down the tower and come into contact with boiling lime water. Free ammonia is thereby produced. The free and volatile ammonium compounds are next caused to pass through a large pipe into the absorption vessel containing sulphuric acid. Here the sulphides and other volatile salts of ammonia are decomposed with the formation of ammonium sulphate and the liberation of hydrogen sulphide and carbon dioxide. These hot gases thus formed are collected in the dome over the absorption vessel and from there pass into the shell of the heating chamber, producing the heat referred to above. The waste sludge from the lime treatment is drawn off from time to time, and the liquor in the absorption vessel is concentrated as it becomes saturated and is sold as crude ammonium sulphate. On recrystallising with lime a pure gas is obtained which being absorbed in water forms aqua ammonia of commerce or ammonium hydroxide of the laboratory.

SYNTHETIC AMMONIA.

Ammonia has also been produced on a commercial scale from a mixture of nitrogen and hydrogen gases subjected to pressure and exposed to a high temperature under the influence of a catalytic agent. According to one process nitrogen is passed through a heated mixture of coal, soda-ash and iron compounded in the form of briquettes; sodium cyanide is thus produced and this on hydrolysis by steaming yields ammonia.

PROPERTIES.

Ammonia is extensively and variously used as a detergent, saponifying agent, in electro-deposition, and in connection with refrigerating appliances, while some of its salts are employed for rendering wood and other materials non-inflammable.

AMMONIUM SULPHATE.

Ammonium sulphate is widely employed as a fertilizer and weed killer. The commercial qualities of sulphate usually contain 0.4 per cent. acid and about 3 per cent. moisture.

There are many processes by which ammonium sulphate can be produced but of late this is produced largely by the process of nitrogen fixation.

On a small scale ammonium sulphate is made by treating finely divided gypsum with ammonium carbonate. Ammonium sulphate is formed along with calcium carbonate.

But on a large scale it is made from ammoniacal liquors as explained under ammonia. The ammoniacal liquor is boiled in a fire-heater until all the ammonium salts are distilled off. The residual liquid containing non-volatile salts is treated with milk of lime and the boiling is continued till all the ammonia is expelled.

When organic nitrogenous materials are destructively distilled, the nitrogen is to a large extent expelled as ammonia and when coal is distilled for coal gas ammonia is a valuable by product obtained in the purification of the gas, and this is an important source of the supply of ammonium compounds.

Formerly the ammoniacal solution was directly neutralised with sulphuric acid, but this method introduced

certain impurities into the product which are injurious to plant life.

On a commercial scale sulphate of ammonia is produced as a by-product in the destructive distillation of coal in the gas work. The liquor is heated to drive off the free ammonia and the vapour is absorbed in sulphuric acid, forming ammonium sulphate, which crystallises sulphate usually containing about 24.5 per cent. of ammonia. It is the common practice in some countries to use only the part of the ammonia which is liberated on distilling the gas liquor alone, but sometimes the fixed ammonia is liberated by the addition of lime.

In practice the gas liquor in gas works as drawn from the condenser is allowed to settle. The settled gas liquor is made to pass through a cylindrical chamber containing a series of narrow tubes heated by steam and also by the waste gases passing through this chamber. The heated liquor is then forced to the top of tall tower where it meets an upward current of steam from a boiler which causes the volatile ammonium compounds such as the carbonate, sulphide and cyanogen to be liberated. The non-volatile or fixed compounds such as the chloride and sulphate flow down the tower and come into contact with boiling lime water. Free ammonia is thereby produced. The free and volatile ammonium compounds are next caused to pass through a large pipe into the absorption vessel containing sulphuric acid. Here the sulphides and other volatile salts of ammonia are decomposed with the formation of ammonium sulphate and the liberation of hydrogen sulphide and carbon-dioxide. These hot gases thus formed are collected in the dome over the absorption vessel and from there pass into the shell of the heating chamber, producing the

heat referred to above. The waste sludge from the lime treatment is drawn off from time to time and the liquor from the absorption vessel is concentrated as it becomes saturated, and sold as crude ammonium sulphate.

In modern times the nitrogen fixation processes are accounting for large amounts of ammonium sulphate. One of these processes is known as Haber process. This consists of the direct synthesis of ammonia from nitrogen and hydrogen, and is carried out by bringing a mixture of the pure gases in the proportion of 1 volume of nitrogen and 3 volumes of hydrogen under a pressure of 200 atmospheres in contact with a catalyst such as iron at about 600°C.

About 8 per cent. by volume of ammonia is produced and this is removed from the gas by washing with water.

Ammonium sulphate is also produced by interaction with calcined gypsum and carbon dioxide. The ground calcined gypsum is put into a vat with water and the washed ammoniacal water from previous operation. Ammonia gas is passed into the suspension until 2-3 per cent. ammonia is in the solution. Carbon dioxide is now passed in at 60°C until the solution contains from 0.3-0.5 per cent. ammonia. The Badische Co. use a suction filter to obtain the solution free from the suspended calcium carbonate which is formed. The Otto process consists of a special reaction column, gypsum and water being introduced at the top, and the ammonia and carbon dioxide are forced in together under pressure at the bottom. The liquid, after filling troughs in the column, flows over and falls to the bottom in the form of a hot saturated solution with calcium carbonate suspended in it.

The mass is cooled, and consists of ammonium sulphate

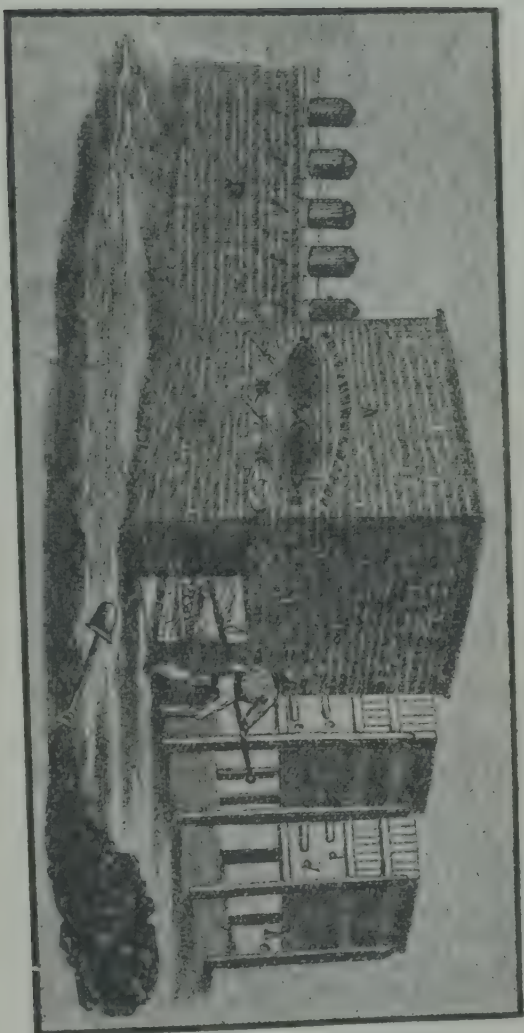


FIG. 16. AMMONIUM CARBONATE MAKING PLANT.

crystals and calcium carbonate. The supernatant liquid is turned to the top of the column with gypsum, and the ammonium sulphate is separated from the mixture by using small amounts of water, filtering, and recrystallising.

AMMONIUM CARBONATE.

Ammonium carbonate, another ammonium compound, is an indispensable article of commerce.

It is now-a-days manufactured by distilling a mixture of calcium carbonate (chalk) and ammonium sulphate. The distillation is carried on in a series of cast-iron retorts set horizontally in a furnace as shown in Fig. Each retort has its mouth, through which the charge is introduced, closed with a moveable door, which is securely fastened in its place, in the manner shown in the figure; and it is furnished at the upper part of its other end, with an iron pipe, to carry off the evolved vapours to the condenser or receiver. The latter consists of two large square wooden chambers (B.C.), lined with lead, and either fitted with moveable covers, secured by leather-joints, or with doors in the side, to permit of the easy removal of the sublimed salt. The first receiver communicates with the second by means of a large leaden tube near its centre, and by another tube, somewhat smaller, and nearer the bottom, but above the surface of the stratum of water in the second receiver, before alluded to. These chambers have also a leaden pipe, stopped during the process with a plug or cock of lead, to allow the liquid product of the distillation, being drawn off, to run into another receiver or cistern, at will.

Both chambers are placed on strong wooden supports or scaffolding, to bring them on a level with the retorts. When the impure sulphate or other ammonia-salt is used

in the manufacture of the sesqui-carbonate (which is usually the case), the resulting salt being impure and coloured is re-sublimed in iron pots, furnished with malleable leaden heads, which are kept cool by a current of air passing over them. A little water is introduced into the subliming pots to render the product translucent. The heat is applied either by means of a flue passing from a retort furnace or by a water-bath heated in the same manner; the latter is the preferable method as the temperature should not be greater than about 90°C . and should not exceed $63^{\circ}-60^{\circ}\text{C}$. These pots are arranged in rows as shown at D in the figure.

The charge of a retort usually consists of about 72 lbs. of sulphate of ammonia (or 57 to 58 lbs. of chloride), to 1 cwt. of chalk; or in proportions thereof. In the above case the product is about 40 lbs. of the carbonate salt, which by careful resublimation, yields about 39 lbs. of marketable carbonate of ammonia.

It is chiefly used for scouring wood; by bakers to lighten their bread; in dyeing; as a general detergent; as smelling-salts and in analysis.

AMMONIUM CHLORIDE.

Ammonium chloride is another ammonium compound largely consumed in this country. It is generally prepared by passing crude ammonia vapour into a saturated solution containing hydrochloric acid. The liquor is then evaporated to the crystallising point, and the crude ammonium chloride purified by sublimation.

The evaporation of the crude saline solution is usually carried on in large square or rectangular cast-iron pans of very moderate depth, and capable of holding from 1000 to 1500 gallons, or more. These are encased

FIG. 18. AMMONIUM CHLORIDE SUBLIMERS.

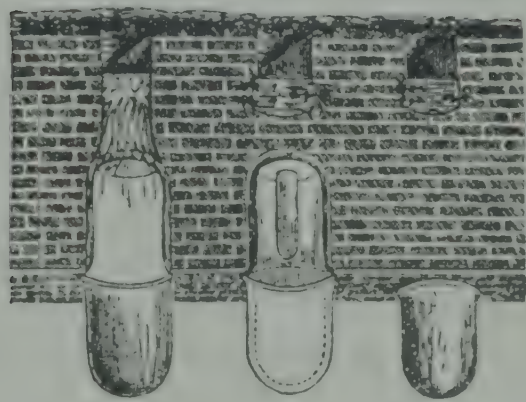
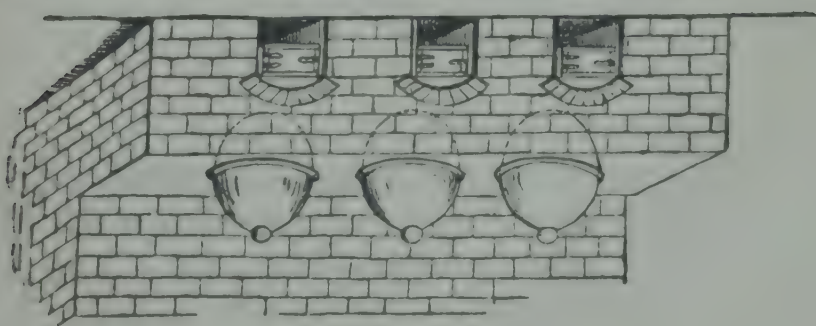


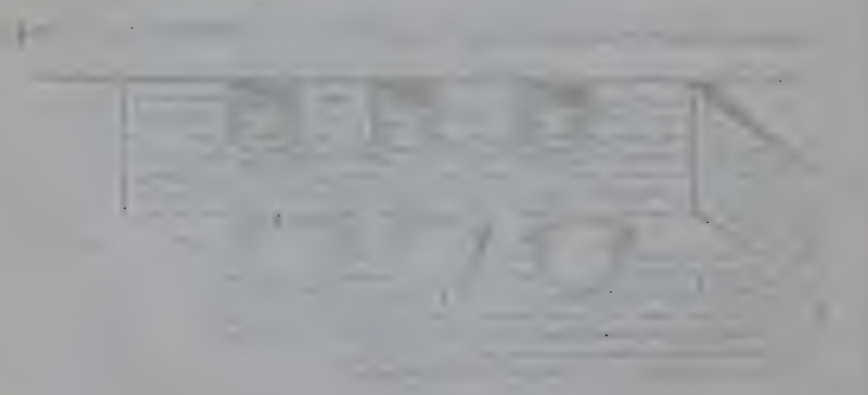
FIG. 17. AMMONIUM CHLORIDE EVAPORATING ARRANGEMENT.





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brickwork, and are heated by a furnace, of which the flues pass in a sinuous course beneath the lining of brickwork in which the vats or pans rest. During the concentration of the liquid, the tar, etc., which separate and float on the surface, and which thus seriously impede evaporation, are from time to time removed by skimming. As soon as the sp. gr. reaches 1.25, any excess of acid in the solution is exactly neutralised with a little fresh ammoniacal liquor, the taste of acid being thus prevented; at the same time any ferric salt present, which would contaminate the ultimate product, is precipitated as sesquioxide. After settling for a short time, the hot liquor is ready to be transferred to the crystallisers.

The vessels employed in the crystallisation are pans or tubs, usually circular and about 7 or 8 ft. wide, by $2\frac{1}{2}$ to 3 ft. deep; these are generally set on the ground, or are bedded either partially or wholly in it. The saline liquor, being pumped or run into them at a little below the boiling temperature, crystallises as it cools, the only interference being occasional stirring or agitation, to prevent the formation of large crystals, which would be inconvenient in the subsequent part of the process. The time occupied in the crystallisation varies according to the size of the crystallisers, and according to the state of the weather, from 3 or 4 to 8 or even 10 days. The 'mother liquor' of the 'crystallisers' is pumped back into the evaporating pans for further concentration.

The crude dried salt of the last process is finally purified by sublimation. For this purpose cast-iron pots lined with clay, and heated from below and by flues round their sides, are employed. The crude grey salt is heated down in these pots until they are about two-thirds filled, when the heads are fitted on, and heat, applied. The latter are

very heavy, being usually made of lead (sometimes iron), and have the form of a dome or a hemispherical cup, with a small tube or hole at the apex, in which a valve is loosely placed, to permit the escape of steam. The domes or heads are so made as to fit closely and firmly to the flat rim or flange of the 'sublimers'; and are retained in their places, during use, both by their weight and by 2 or 3 clamps provided for the purpose. They are furnished with 3 rings, set at equal distances, to allow of their being lifted off, or moved, by means of a pulley and chains. The due application and regulation of the temperature is here of the utmost importance. If the temperature employed be too high, the sublimed salt will be contaminated with empyreumatic matter while some of it will be carried beyond the dome and lost; and if it be extremely high the head may be blown off altogether and the contents of the pan scattered about the building; whilst on the other hand, if the temperature employed be too low, the resulting cake of sal-ammoniac will be soft, spongy, and either grey or yellowish.

The proper temperature is said to be known by 2 or 3 drops of water boiling readily and being dissipated as vapour, when placed on the head or cover of the sublimers; but it should not 'spit' or 'dance about' or be raised by the heat out of contact with the metal. The usual practice is to keep the fires 'briskly up until the sublimers and their surroundings attain a sufficient degree of heat, when they are slackened, and maintained at a mean temperature" (Muspratt). The sublimation occupies from 5 to 9 days; but it is customary to raise the heads once or even twice a week, to ascertain the progress made, the fires having been purposely neglected or checked for some hours previously. The process is finally stopped

Before the whole of the crude salt in the pots is volatilised, otherwise the heat required for that purpose would lead to the decomposition of the carbonaceous impurities, and cause them to emit volatile hydrocarbons, which would materially lessen the purity and beauty of the product. The unsublimed portion in the pots forms a conical mass, called the 'yolk.'

It is used in the arts, chiefly in the coating and soldering of metals, the preparation of freezing mixtures and in dyeing. It gives pungency to snuff.

It is one of the ingredients required for the manufacture of nitric acid. It is also a component of gun powder. With the increasing production of nitric acid and gun powder the demand for this stuff is bound to increase. The method usually followed is usually crude. The yield is consequently poor and the product is full of impurities. The following process is simple and up-to-date. It will increase the yield of greater purity.

CHAPTER XXI.

SODIUM & POTASSIUM COMPOUNDS.

POTASSIUM NITRATE.

SALTPETRE earths are found in various parts of India chiefly in the United Provinces and Bihar which are the most important ones in this respect, and whence nearly all the natural saltpetre is still derived.

The raw material is mostly a product, continually reformed by the action of atmospheric air upon nitrogenous organic matter in the presence of bases, such as lime, magnesia, and potash. The organic nitrogen is simply oxidised by atmospheric oxygen; the process of nitrification never takes place except in the presence of microbes. Saltpetre earth is, therefore, chiefly found in the neighbourhood of villages where urine, etc., yields an abundant supply of organic nitrogen. In Bihar, it is collected partly from the soil by scraping off the uppermost layers which show a white efflorescence.

EXTRACTION.

The impure saltpetre earth thus collected is lixiviated in earthenware dishes or wooden boxes or in pits dug into the ground and made tight by a clay puddle. The liquor is concentrated in iron pots or sometimes only by solar heat and a crop of every crude saltpetre is obtained.

Before submitting the liquor to the process of concentration, it is thoroughly mixed with wood ashes, which generally contains carbonate of potassium. The advantage

ge of adding the wood ash is to convert the whole of calcium and magnesium nitrates present in the crude product into insoluble carbonates. The solid residue is then separated either by filtration or by decantation and the liquor thus obtained from the clarified liquor by slow evaporation in earthenware pots is the saltpetre of commerce containing 45 to 70 per cent. of potassium nitrate.

REFINING OF SALTPETRE.

The saltpetre obtained by the above process contains several impurities, the most troublesome of which are the chlorides. Since saltpetre is mainly utilized in the manufacture of gun-powder and fire-works, it is absolutely necessary to remove the objectionable chlorides, because they readily absorb moisture and thus spoil the whole. The usual method adopted by the manufacturer is stated thus:—

In an iron pan 1050 lbs. saltpetre is dissolved in 600 lbs. of water at a gentle heat; the solution is brought to boiling heat, and another 188 lbs. of saltpetre is dissolved in it. When employing these proportions with saltpetre containing about 20 p.c. of chlorides, the nitrate is dissolved completely, but the chlorides partially. The latter is skimmed out with a perforated ladle. If calcium or magnesium salts are present, potassium carbonate is added until a fairly alkaline reaction has been produced. The hot clear liquor is diluted with 300 lbs. of water, a solution of 1 lb. of glue dissolved in 44 lbs. of hot water is stirred into it, and the whole brought to boiling again. The glue combines with organic substances present forming scum which rises to the surface and is carefully removed. When the scum rises to the surface, the liquor is allowed to settle for 24 hours in a warm place and the clear portion is run

into flat copper coolers. As soon as the crystallisation begins, the liquid is constantly stirred, either by hand or better by machinery. Thus the potassium nitrate separates as minute, floury crystals. These are drained and cold water is sprinkled over them to remove all adhering mother liquor. This is usually done in vessels provided with a perforated false bottom, covered with linen. Finally the floury particles are dissolved in a small quantity of hot water and then set aside to cool without disturbing, when large crystals of saltpetre begin to appear. It is a valuable fertiliser.

POTASSIUM PERMANGANATE.

FIRST METHOD.

The permanganate of potash is made by fusing with a strong heat a mixture of equal parts of peroxide of manganese and hydrate of potash, or one part of peroxide and two parts of nitre. The mass is to be dissolved in water, and if the solution is green, it should be reddened by the cautious addition of a few drops of nitric acid. The clarified liquor is to be evaporated to the point of crystallisation. Even the smallest crystals of this salt have such an intense red colour that they appear black with a green metallic reflection. In the air they gradually assume a steel-grey hue without undergoing any essential change of nature. The least portion of any organic matter added to the solution of this salt reduces the permanganic acid to the state of peroxide, which precipitates being combined with water; the liquor becomes green or colourless according to circumstances.

SECOND METHOD.

A more permanent permanganic salt may be made as follows:—Melt chlorate of potash over a spirit lamp

and throw into it a few pieces of hydrate of potash, which immediately dissolve and form a limpid liquid. Then peroxide of manganese in fine powder is gradually introduced into that melted mixture; it immediately dissolves, with the production of a rich green colour. After adding the manganese in excess, the whole is to be exposed to a gentle red heat, in order to decompose the residuary chlorate of potash. It is now a mixture of manganate of potash, chloride of potash and peroxide of manganese. It still shows a deep green coloured solution, which when heated assumes a fine red colour, in consequence of its becoming a permanganate, and it ought to be decanted from the sediment while hot. By cooling, the permanganate of potash separates in crystals possessed of great lustre; and towards the end colourless crystals of chloride of potassium are deposited.

POTASSIUM FERROCYANIDE.

This yellow-coloured salt, generally known as yellow prussiate of potash, is a very important substance. It is prepared on a large scale by igniting such carbon as contains nitrogen to a red heat with potassium carbonate in closed vessels. The quantities of the materials may be varied, the relative proportions being given by some makers as 100 parts of potassium carbonate to 75 parts of the nitrogenous carbon, or according to Runge, 100 parts of potassium carbonate, 400 of torrified horns and 10 parts of iron filings. The nitrogenous materials used are horns, hoofs, blood, wool dust, cuttings of hides, and leather.

The fusion of these ingredients is carried on either in closed iron vessels of a peculiar shape, or in a reverberatory furnace. The iron-vessel, termed a muffle, is

egg or pear-shaped, having a diameter of 1.2 metres and varying from 12 to 15 metres in thickness, with a short, wide neck in front. The iron vessel is placed in the furnace in such a manner as to be exposed to the action of the flame and hot gases on all sides, being supported at the back by a brick pier about 27 centimetres long, and resting on bricks, leaving space sufficient for the gases generated in the interior to pass off by a channel into the chimney. During the operation of melting the opening at the front, through which the charge is put or the molten mass withdrawn from the vessel, is provided with damper. A shallow pan is also placed on the top of the furnace for the evaporation of the liquor obtained by treating the molten mass with water. The use of iron vessel, however, is attended with the serious drawback because the iron is eaten away in holes in a comparatively short space of time; and to prevent this action is greatest on the lower part of the vessel, it may therefore be turned bottom upwards, and the opening stopped with fire-clay, the vessel has soon to be replaced by another. It is on this account, and also owing to the fact that a larger quantity of raw material can be operated upon at once, that there has come into general use the reverberatory furnace. The fused mass is then dissolved in water and evaporated to make volume from which the crude salt crystallises. The salt is next purified by recrystallisation, while the black residue is employed as manure and for decolourising paraffin, etc.

POTASSIUM CARBONATE.

Impure potassium carbonate has been known since very ancient times. Its principal source in this country is wood ashes because potash is an indispensable element

for the growth of most plants. But where it is associated with much silica and phosphoric acid, the ashes contain little carbonate, and are not available for the manufacture of potash. This, for instance, holds goods of straw-ash. The value of an ash for the manufacture of potash is chiefly dependent upon the quantity of postage carbonate it will yield, upon the abundance of the wood or other vegetable product and the cost of labour.

The under-mentioned woods yield on the average, for 1000 parts, the following quantities of potash:—

Pine	0.45
Beech	1.45
Oak	1.53
Willow	2.85
Wheat straw	3.90
Barley straw	5.80
Vine-wood	5.50
Stems of maize (Indian Corn)	6.50
Sunflower stems	20.00
Dried Wheat Plant	
previous to blooming	47.00

FROM WOOD ASH.

Potassium carbonate or pearlash may be commonly obtained from wood ashes but it can also be manufactured by LeBlanc's process as adopted in the manufacture of soda ash. In making potassium carbonate from wood ashes the following procedure may be adopted. The wood such as, pine, oak, beach, vine stalks, etc., is burned in pits dug in the earth. The collected ash is spread on a stone floor, sprinkled with water, and worked through until it is evenly damp. A little lime is sometimes mixed with it.

which afterwards causes the formation of caustic potash. The damp ash is placed in casks provided with a false bottom, covered with straw, and hot water is poured over it. After some time the liquor thus formed is drawn off by a plug hole at the bottom; if it is about 32°Tw strong it can be boiled down at once; the weaker liquors and washings are used for lixiviating fresh ash.

The boiling down is a very rough process. In lieu of pans possessing a large heating-surface usually circular cast-iron pots fired from below are employed, in which the liquor is boiled down to dryness. In spite of stirring up the mass before it becomes quite dry much of it burns fast to the pot, causing a great waste of fuel and a speedy destruction of the pot. The potash thus obtained contains many impurities.

In order to get pure carbonate of potash two different methods are followed. In one the carbonate is stirred up in an iron pot with $1\frac{1}{2}$ or 2 times its weight of cold water, and the mixture which gets hot is allowed to cool down before syphoning of the clear liquor. The sulphate and some chloride remain behind, together with the insoluble matter; the residue is not washed (which would cause the sulphate to be re-dissolved); but is only pressed. The liquor, containing mostly carbonate, but also chloride and silicate, is brought to dryness, stirring it up to the end. In the other method the solution is made with hot water, the residue is exhausted in the way, the liquors are boiled down to sp. gr. 1.50 and allowed to cool, when the sulphate and some chloride crystallise out. This process is rather more expensive than the former.

THREE STAGES IN PREPARATION.

The preparation of potash from vegetable matter is effected in three operations, viz. —

- (1) The lixiviation of the ash
- (2) The boiling down of the crude liquor
- (3) The calcination of the crude potash.

The combination of the vegetable matter should be conducted as to prevent its becoming too violent and giving rise to the volatilisation of some of the reduced potash nor should too strong a current of air be admitted, for fear of the ash being mechanically carried off.

LIXIVIATION OF ASH.

The lixiviation of the ash effects the separation of the soluble from the insoluble saline matter. The operation is carried on in wooden vessels provided with perforated false bottom, which is covered with straw; in the real bottom a tap is fixed for removing the liquor. The ash to be lixiviated is first sifted from the coarse particles of charcoal, next put into a small square water-tight wooden box, and thoroughly saturated with water for at least 24 hours. By this procedure the lixiviation is greatly assisted, and the potassium silicate is to some extent decomposed by the action of the carbonic acid of the atmosphere. The next step is to transfer the wet ash to the lixiviation vessel, care being taken to press it tightly down to the false bottom; cold water is then poured in, until the liquor begins to run off at the tops left upon for that purpose. The liquor which runs off after the water has remained some little time in contact with the ash, is found to contain about 30 per cent. of soluble salts, afterwards decreasing to about 10 per cent. when hot water is employed to complete the lixiviation. The insoluble residue left in the lixiviation tub is of value as a manure. on

account of the phosphate of lime it contains, and is also used in making green bottle glass.

BOILING DOWN THE LIQUOR.

The liquor obtained by lixiviation is of a brown colour, owing to organic matter. The evaporation is carried on in large shallow iron pans, fresh liquor being added from time to time; and the operation is continued until a sample of the hot concentrated liquor exhibits on cooling a crystalline solid mass.

When this point is reached the fire is gradually extinguished, and as soon as the contents of the pan are sufficiently cold to handle, the solid mass is broken up; its colour is a deep brown. The crude product may contain 6 to 12 per cent. water.

CALCINING THE CRUDE POTASH.

When all the water is to be expelled the saline mass is calcined. A calcining furnace is a type of reverberatory furnace provided with double fire place. The crude potash, broken to egg-sized lumps, is next placed in sufficient quantity in hearth. The first effect of heat is to expel the water from the potash, the escape of the steam being promoted by stirring the mass with iron rakes. In about an hour all the water is driven off, and the mass takes fire in consequence of the burning of the organic matter. The salt is at first blackened, but gradually becomes white as the carbon burns off. As soon as this stage is reached, the potash is removed to the cooling hearth, and when cold packed in well-made wooden casks. The heat of the furnace has to be well regulated to prevent the potash becoming semi-used, in which case it would attack the silicious matter of the fire bricks; the

operator from time to time takes a small sample to test how far the calcination is complete.

SODIUM SILICATE.

Sodium silicate is generally known in the market by different names. To the soap makers who are at present the largest consumers for the detergent agent combining moreover a hardening effect on soap, it is known as silicate only. Cotton mills, the next good consumers, call this by water glass. To the artificial stone makers it is termed as soluble glass. There are many a variety of uses of this chemical and the demand is daily increasing. Recently it is used very successfully in the mortar of building and is gradually replacing the use of asphaltum and tar products in road making.

Industrially, silicate of soda is prepared by wet and dry methods as given below:—

WET METHOD.

The wet method is much used because of the greater uniformity of the product, and because it is obtained in solution at once. It consists of digesting silica 28 parts—preferably infusorial earth—with a solution of caustic soda of sp. gr. 1.22-1.24 (prepared by causticising a solution of sodium carbonate with lime) containing 1 part of caustic soda, under three or four atmospheres' pressure. The liquid is heated by blowing steam, and is kept stirred by machinery. Complete solution is attained when a sample withdrawn from it shows that the suspended matter settles rapidly and is of a brick red colour whilst the liquid is almost free from alkaline reaction. This takes about 3 hours. The caustic soda must not be above 1.24 sp. gr. as a stronger solution holds the fine sand and

ferric oxide in suspension for a long time, such solution not clarifying properly even after standing for several days. The clarified liquid is drawn off; it has a sp. gr. of 1.18, the decrease being due to the dilution produced by the condensed steam. Instead of infusorial earth, other forms of silica, such as powdered flints, quartz, etc., can be employed, but the digestion must then be continued for a longer time and under 7-8 atmospheres' pressure. The clear solution is then concentrated in iron pans to the required strength usually 1.7 sp. gr.

DRY METHOD.

The dry method which is quite simple consists of a mechanical mixture of silica sand, soda ash, having 5 per cent. alkalinity. The whole of this is then put into the furnace already heated to more than 800°C , and continued to burn 5 to 6 hours. The resultant obtained is a fused mass and drawn out by ladles and allowed to cool to a certain degree.

Sodium sulphate is sometimes used in place of sodium carbonate in which case coal is added to assist in the reduction of the sulphate.

Typical mixtures follow:—

I.

Powdered quartz	100	lbs.
Calcined sodium carbonate	28	lbs.

II.

Powdered quartz	100	lbs.
Calcined sodium sulphate	60	lbs.
Coal	15-20	lbs.

III.

White sand	180	lbs.
Sodium sulphate	100	lbs.
Coal	10	lbs.

IV.

White sand	180	lbs.
Sodium carbonate (50%)	100	lbs.
Coal	3	lbs.

V.

Sand	100	lbs.
Sodium carbonate	56	lbs.

VI.

Sand	100	lbs.
Sodium sulphate	70	lbs.
Wood charcoal	4	lbs.

VII.

Silica sand	480	lbs.
Soda ash (56-68%)	448	lbs.
Charcoal	40	lbs.
Borax	1½	lbs.

The amount of coal necessary with the sodium sulphate is only that required to convert it into sodium sulphite, since this reacts readily on the silica, and further deduction may be made for the smoke from the furnace gases.

The coal in the formula No. 4 is added to reduce the sodium sulphate present in the low grade impure sodium carbonate there used. The coal added should not be sufficient to further reduce sulphite to sulphide, as this hinders the formation of the silicate. The coal, charcoal or saw-dust are well mixed with the sulphate, and the mixing is

continued while the sand is added. A Siemen's regenerator furnace 10 ft. by 30 ft. will make about 22 tons of water-glass in 24 hours with a consumption of 5 tons of fuel. The formation from sodium sulphate is more difficult and slower than from sodium carbonate.

Before a new furnace is used for making sodium silicate, a charge of bottle glass should be made in it so as to subsequently protect the brickwork. The temperature required is about 1100°C and the time 5 to 8 hours. When the charge is fused a portion only is drawn from an upper tapping hole, and the furnace with its part charge of molten silicate is then recharged with fresh raw materials.

Smaller reverberatory furnaces with ordinary firing are very successfully used, and their output is about $1\frac{1}{4}$ tons per day.

The run-off fused product after cooling is sometimes colourless, but usually has a brownish or greenish colour due to iron; it is broken up by a stone breaker, and ground by suitable machinery.

SODIUM SILICATE SOLUTION.

Water-glass is nearly insoluble in cold water, but dissolves completely, although slowly, in boiling water, the solubility decreasing as the percentage of silica in the substance increases. Commercially the crushed or powdered water-glass is dissolved by long boiling with water, preferably under pressure. The resulting solution is allowed to clarify, and is then evaporated to 40°Be , in iron pans. The small proportion of sulphide sometimes present from the reduction of the sulphate can be removed by adding a little copper scale or litharge when preparing the solution. 100 lbs. of the solid yield about 300 lbs. of a solution of 40°Be . Maety treats the broken

water-glass in the dissolving drums with steam at about atmospheres pressure, whilst the drums rotate at about revolutions per minute, the solution process taking about 6 hours. The capacity of the drums should be in the proportion of 1 litre to 1 kilo. of dissolved glass, so that, the sp. gr. of the water-glass being 1.5, the drum is two-thirds full at the end of the process. For each kilo of solid glass about $1\frac{1}{2}$ to 2 kilos of steam is used. When solution is complete the product is run off into settling tanks, and after the mud has settled, passed through a terpress. The clear water-glass so obtained generally has to be concentrated. This is carried out into a vacuum pump, the solution being stirred during concentration to obtain a homogeneous product.

The aqueous solution of sp. gr. 1.7 usually has the following composition; silica 32.33 p.c., soda $16-16\frac{1}{2}$ p.c., other sodium salts $2\frac{1}{2}-3$ p.c.

PURE SILICATE.

A pure silicate may be made from the crude product by passing a current of carbon dioxide through the solution, filtering off the precipitated hydrated silica, and dissolving it in caustic soda.

CAUSTIC SODA.

Caustic soda is an essential raw material for soap manufacture, being the agent used for saponifying the fats and oils. It is also used in many other important industries such as paper, mercerised cotton, artificial silk, explosives, dyestuffs, etc.

Caustic soda can be manufactured in various ways, which the following processes are more or less important:—

- (1) From Reh.
- (2) By the electrolysis of brine.
- (3) By causticising sodium carbonate with lime.
- (4) By sodium Ferrite Process.

CAUSTIC FROM REH.

In India a kind of earth is available. It is known as reh or sajji mainly composed of sodium carbonate and sulphate. It is deposited in the soil of many parts of United Provinces, the Punjab, Sind, and Madras. The deposits are very extensive and offer good prospects for commercial extraction. In the opinion of many chemists this indigenous source of alkali is not so negligible as has been hitherto assumed but is easily capable of meeting the whole of India's requirements of caustic soda.

The process of making caustic soda from reh has been developed by Messrs. Watson & Mukherjee of the H. B. Institute, Cawnpore. By the help of this process caustic soda of European standard can be produced by causticising crude reh salts. The process is as follows:—

500 parts of sajji (reh) is dissolved with 2600 parts water; and $183\frac{1}{2}$ parts of freshly prepared lime (calcium oxide) dissolved with three times of its weight of water is added to the boiling reh solution gradually with vigorous stirring. By this treatment about 92.4 per cent. of carbonate present in the reh is converted into caustic soda, the specific gravity of the resulting liquor being 23°Tw . The clear liquor is next separated from the lime mud and concentrated. As the reh contains some appreciable amount of sulphate of soda it is first crystallised out because it is less soluble than caustic soda. The crystals which first forms is mainly sulphate and is removed. The mother liquor which is now almost free from sulphate is

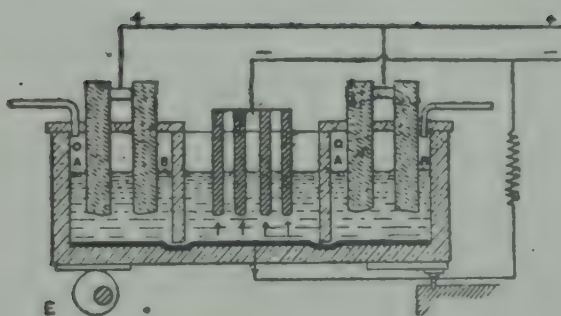


FIG. 19. CAUSTIC SODA PLANT.

further concentrated and ultimately evaporated to dryness in nickel vessels. The substance thus obtained is finally fused over moderate fire. In this way a practically colourless caustic soda may be obtained, the organic matter present being destroyed during fusion.

An analysis shows that the mass contains the following:—

Sodium hydroxide	78.50 per cent.
„ carbonate	15.11 „ „
„ sulphate	1.03 „ „

Note:—15 tons of practically pure sulphate of soda are obtained as a bye-product.

ELECTROLYTIC PROCESS.

In the electrolytic process solution of sodium chloride (brine) is used as raw material. The apparatus devised by Castner for this purpose is shown in the Figure. It consists of a rectangular vessel divided into three compartments. Upon the floor of the vessel there is a layer of mercury about $\frac{1}{8}$ th of an inch deep. The partitions, which are non-porous dip into narrow gutters across the bottom, but do not actually touch the bottom, so that when the tank is gently oscillated the mercury can flow from one compartment to the other, while the liquid above is prevented from so doing. The two outside compartments are filled with brine, while the central one contains water; and in this is placed the cathode, consisting of a number of metal plates. Since the partitions are non-porous the current will pass from the carbon anodes through the salt solution to the mercury, which in the two extreme compartments then becomes the cathode. It then passes from the mercury in the middle space, which now becomes the anode of this cell, through the aqueous liquid

to the metal cathode which is there suspended. In the outside compartments the sodium chloride is electrolysed, the chlorine discharged at the carbon anodes escapes by the pipes, while the sodium dissolves in the mercury cathodes. During the process a slow rocking movement is given to the tank by means of the eccentric represented at E, whereby the mercury is caused to flow to and fro along the bottom. In the middle compartment the sodium contained in the amalgam is transported to the cathode, where it dissolves in the water, forming sodium hydroxide.

Another important apparatus known as the Diaphragm cells is erected in various Continental factories. In these cells there is placed between the anode and cathode a diaphragm which allows the ions to pass through by electrical migration but reduces the diffusion of electrode products towards each other.

Diaphragms are generally made of asbestos, commonly of asbestos paper, ranging in thickness from 0.01 to 0.05 in.; and are placed near or in contact with the cathode. The cathode may be made of iron gauze or perforated sheet iron and the anode, of carbon or graphite or of magnesite.

Cells may be constructed with vertical or horizontal diaphragms. In cells with horizontal diaphragms the cathode is placed horizontally in the cell with the anode above it. Vertical diaphragms seem to be preferred; they allow greater accessibility and greater compactness, and sediment, instead of settling on the diaphragm, falls to the bottom of the cell. In horizontal diaphragms, however, the diffusion is more uniform, for the hydrostatic pressure is distributed evenly over the whole diaphragm.

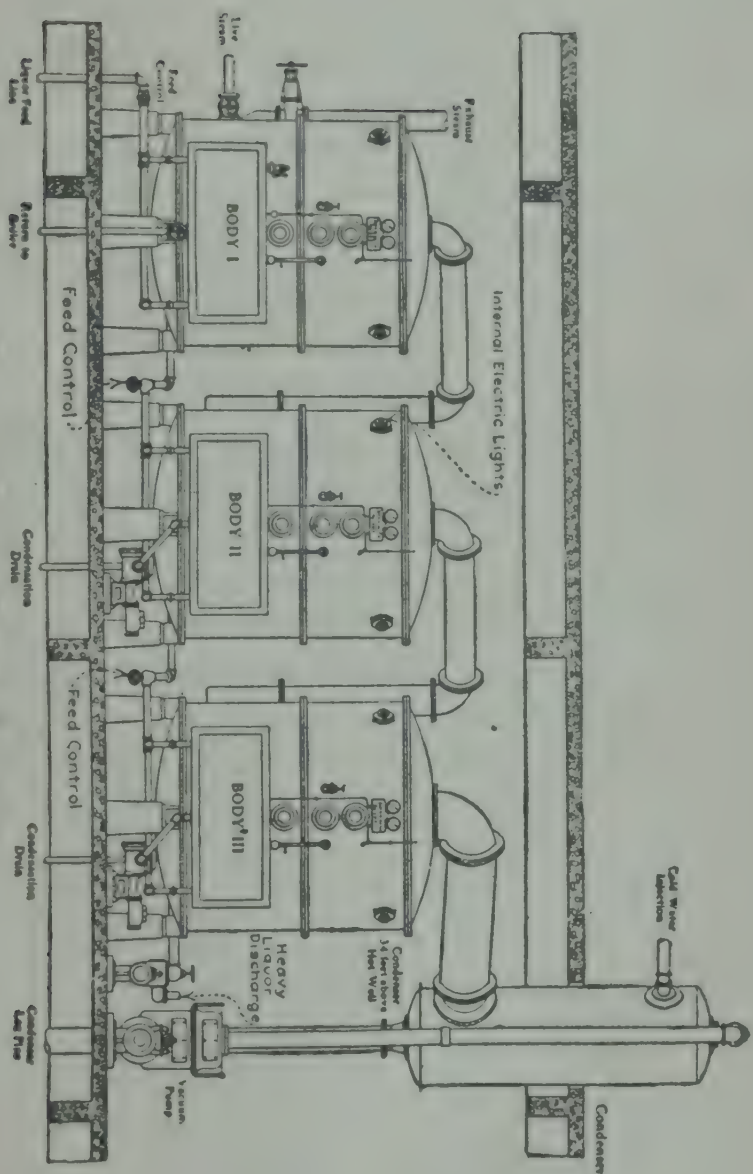
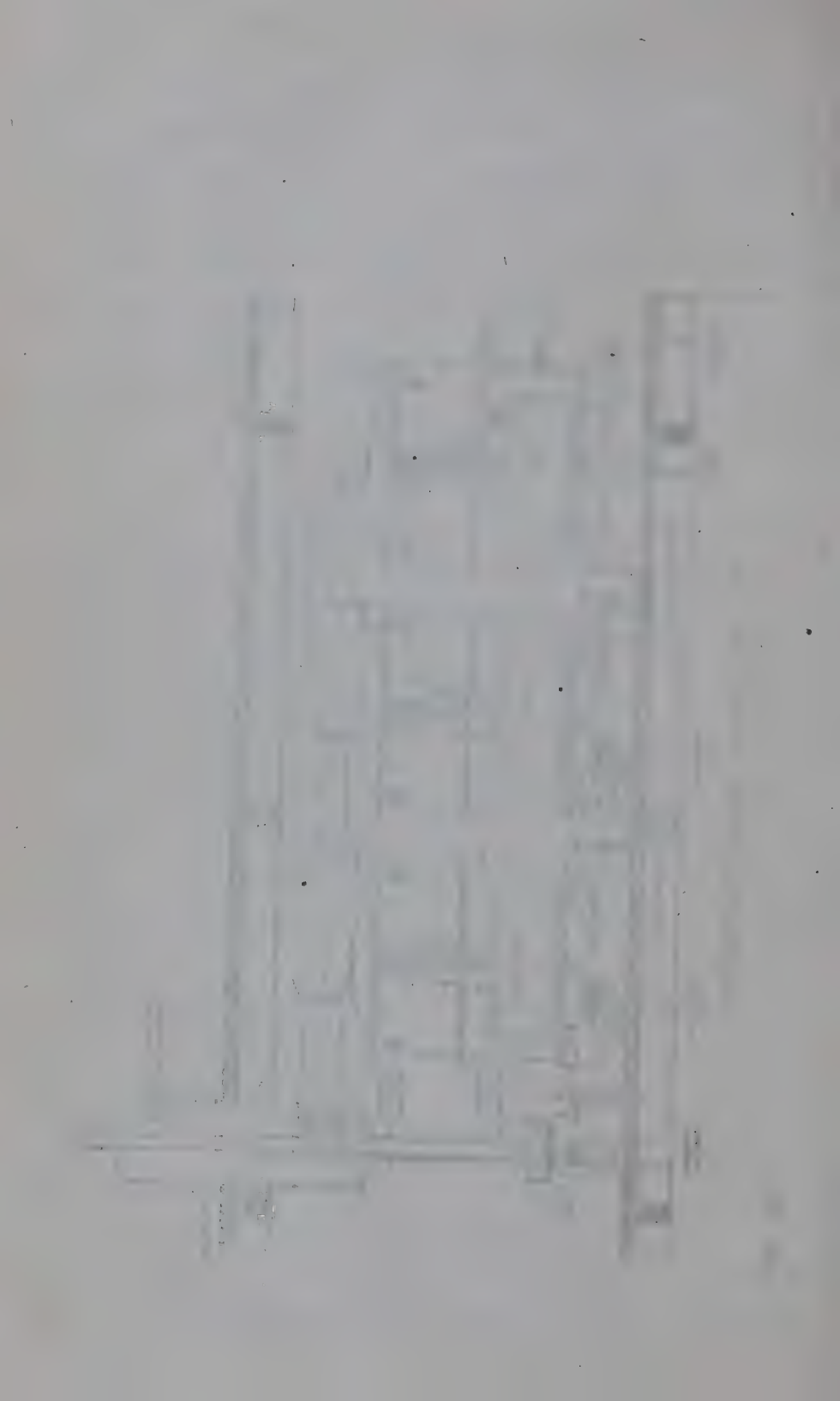


FIG. 20. TRIPLE EFFECT EVAPORATOR.



In both horizontal and vertical diaphragm type of cell the diaphragm is replaced periodically as it sometimes clogs.

Diaphragms permit the construction of compact cells, for the electrode can be placed fairly close together; but the diaphragms on account of their resistance, require a higher voltage and higher hydrostatic pressure on the brine feed. They may not always be uniform in thickness or in porosity, so that, when the hydrostatic pressure is properly adjusted for one part of the diaphragm the rate of brine flow may be too high or low at the other parts.

EVAPORATING CAUSTIC LIQUOR.

The customary practice is to evaporate the caustic liquor obtained from the cells in vacuum pans or evaporators. These may be single, double or triple effect depending upon the size of the plant. The sodium chloride is less soluble than the caustic soda and as evaporation proceeds the former crystallises and settles at the bottom. The salt and some caustic liquor is returned to the evaporator. The concentrated solution is further evaporated in a single effect evaporator, where it is concentrated to a caustic content of 50 per cent. and small amount of salt. On passing this solution through the cooling apparatus more salt crystallises, but the salt content, until recently, could not be reduced below 16 or 17 per litre by evaporation. Much of the caustic is marketed as a strong caustic solution containing 50 to 55 per cent. sodium hydroxide.

If it is desired to reduce the salt content further, the 50% strong liquor is slightly diluted so that it becomes unsaturated with respect to sodium chloride. It is then cooled until the caustic but not the salt crystallises. The

caustic crystals are filtered free from salt and are finished as solid sodium hydroxide.

In most cases 2 per cent. or less of sodium chloride is not objectionable. Therefore, the strong caustic liquor is run into large cast-iron pots for evaporation to dryness. The pots are heated by coal, oil or gas. When all the water has been evaporated and the caustic lies in a quite molten state, sulphur is added to clarify the liquid, which consists mainly in the removal of iron. The molten caustic is then run into steel drum of required sizes.

The strong liquor may also be passed over flaking drums for producing flake caustic.

The brine enters the cell at a concentration of 30 per cent. sodium chloride. This is reduced to 20 per cent. in its passage through the end compartments. It leaves these compartments and passes to a concentrating tank, where the sodium chloride content is brought up to 30 per cent. Any sodium sulphate, calcium salts, and iron salts must be removed from the brine; because they will destroy the graphite electrodes and decompose the amalgam of sodium and mercury.

The middle compartment is provided with a water inlet and a hydrogen outlet and a caustic outlet.

In the passage of the current through the cell, chlorine is liberated in the outer compartments and also the sodium. The sodium does not combine with water to form sodium hydroxide and hydrogen, but dissolves in the mercury in the mercury cathode.

Since the cathodic efficiency in the outer brine compartments is less than 100 per cent., some of the current would have to leave the mercury in the middle compartment in some other way than by forming sodium ions. The result is that some of the current that enters the middle

compartment form mercury ions unless this is prevented by some means. This formation of mercurous ions is avoided in practice by shunting part of the current around the middle compartment. The amount of current to be shunted is equal to that which would be used in the formation of mercury ions; in commercial practice it amounts to about 10 per cent.

The sodium leaving the mercury in the middle compartment and combining with the water involves a decrease in free energy. This results in a saving of voltage, for the actual voltage applied across the terminals of the cell is equal to that required to decompose the sodium chloride in the outer compartments minus that generated in the middle compartment. The total electromotive force across the cell is 4.1 to 4.2 volts.

The sodium on entering the mercury in the outer compartments would diffuse toward the middle compartment. The rate of diffusion of sodium in undisturbed mercury is too low for commercial work, because much sodium will accumulate in the amalgam making it very viscous. But in carrying out the operation successfully this high concentration of sodium in amalgam must be kept low in order to avoid liberation of hydrogen.

In order to maintain the efficiency of the cell the sodium content of the amalgam is kept below 0.2 per cent. For the purpose the cell is rocked mechanically. One end is pivoted and the other end is raised and lowered by a cam about an inch each minute.

Each cell consumes 6.30 ampere at 4.2 volts and has a current efficiency of 50 to 95 per cent. The yield, based on the current efficiency and operating voltage, is 0.71 gram sodium hydroxide and 0.65 gram chlorine per kilowatt hour.

The solution in the middle compartment contains about 240 grams sodium hydroxide per litre.

In the construction of each cell a little over 100 lbs. of mercury are required.

PREPARATION OF BRINE.

The brine used is usually a saturated solution of sodium chloride. This may be obtained by dissolving sea salt. The sea salt is placed in a dissolving tower in which water is admitted from the bottom and leaves at the top. The rate of flow is so adjusted that the water becomes saturated by the time it leaves the tower.

Although the salt used is fairly pure, it is necessary to remove the small amounts of calcium salts usually present. Sometimes magnesium salts may also be present in sufficient amount to require removal. To remove these the saturated brine is treated with a small amount of soda ash solution. The calcium and magnesium carbonates formed are allowed to settle, after which the clear brine is treated with hydrochloric acid in another tank to neutralise the excess of sodium carbonate.

If too much sulphate is present in the salt, it should be removed by precipitation with barium chloride solution otherwise its electrolysis results in excessive oxidation of the anodes and an abnormal increase in the percentage of carbon dioxide in the chlorine.

After the separation of calcium and magnesium compounds and also the sulphates, if any present in the salt solution, the brine is diluted to 30 per cent. strength, as this strength of brine is actually put into the cells, which is mentioned in the process.

CURRENT EFFICIENCY.

The current efficiency of the cells is determined by dividing the actual amount of sodium hydroxide or chlorine produced per unit of time by the theoretical maximum that could be produced according to Faraday's laws (i.e. Electro Chemical equivalent). For sodium hydroxide the theoretical maximum is 3.29074, for chlorine it is 2.91626 lbs. per 1000 amp-hour.

E. for Caustic production.

$$X \times 100$$

$$= \frac{\quad}{3.29074} \text{ per cent,}$$

where X = lbs. of caustic produced per 1000 amp-hour

E. for Chlorine production

$$Y \times 100$$

$$= \frac{\quad}{2.91626} \text{ per cent.}$$

where Y = chlorine produced per 1000 amp-hour

ENERGY EFFICIENCY.

The energy efficiency is equal to the product of the decomposition potential of sodium chloride and the current efficiency, divided by the operating voltage of the cell. The decomposition potential of sodium chloride can be taken as 2.3

$$\text{Energy Efficiency} = \frac{2.3 \times C.E. \times 100}{\text{operating voltage.}} \text{ per cent.}$$

PRODUCTION PER KILOWATT-HOUR.

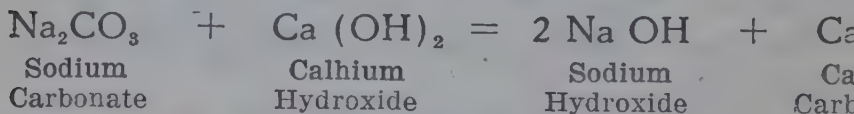
For sodium hydroxide and chlorine, the actual production per kilowatt hour is equal to the product of the

theoretical production per ampere-hour the current efficiency, and 1000 divided by the operating voltage of cell, thus:—

$$\begin{aligned} & \text{Pound of Caustic per Kw.-hr.} = \\ & \quad \frac{X \times 1000 \times \text{C.E.}}{\text{operating voltage.}} \\ & \text{(where X = Pound of caustic per amp. hr.)} \\ & \quad \frac{3.29074 \times \text{C.E.}}{\text{operating voltage.}} \\ & \text{Pound of chlorine per kw-hr.} \\ & \quad \frac{2.91626 \times \text{C.E.}}{\text{operating voltage}} \end{aligned}$$

CAUSTIC SODA FROM SODIUM CARBONATE.

This process may be employed by soap maker saponifying fats and oils at this time when the solid caustic is extremely difficult to procure and also its price is orbitantly high. Here sodium carbonate is boiled with milk of lime to effect the chemical reaction, as given by following equation:—



The soda solution which is made upto a sp. gr. of 1.25 is causticised in large tanks with a flat bottom. The solution must be heated to 190° to 200°F with vigorous stirring. Now milk of lime having a concentration of 100 grams of CaO (lime) per 1000 grams is added. When the causticising is complete decantation of the supernatant caustic solution is done through the outlet attached to

de' near the bottom of the tank. After sufficient lime is added and the desired conversion is obtained, the liquor is allowed to settle for about 2 hours. The clear portion is drawn off and the lime sludge is washed with hot water. After settling, clear liquor is filtered off and mixed to the first liquor. This process is repeated for three or four times. The wash of third and fourth operation must not be mixed with the lye obtained in first and second wash. These must be used as the second and third wash water in next charge. The washed lime containing the precipitated calcium carbonate is thrown away. The time taken for this complete operation is about 16 hours.

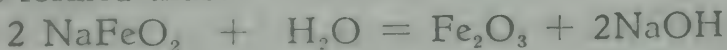
CAUSTIC SODA BY SODIUM FERRITE PROCESS.

Another method of preparing caustic soda is the sodium ferrite process.

Calcined sodium carbonate or crude bicarbonate is mixed with iron oxide (Fe_2O_3) in a rotating cylindrical furnace and heated to redness by the hot gases from the furnace passing through it. Sodium ferrite NaFeO_2 is formed thus:—



The product is then treated with water, when the iron oxide is regenerated (and used again) and caustic soda is formed thus:—



The lye obtained from the liquor tank is concentrated and must be brought about 45°Be . The liquor is then drawn out and kept in settling tanks where salt and soda separate out, these two being sparingly soluble in caustic solution at this concentration. It is now filtered and the purified caustic is heated on an open cast iron pot by the direct fire and the temperature is gradually raised until

it reaches above 400°C . At this temperature the mass quietly boils and a dark scum of graphite may be seen, and ferrous oxide oxidised to ferric oxide Fe_2O_3 which settles to the bottom. The molten mass is allowed to settle and ladled out into steel drums to solidify. The mass solidifies on cooling and the drum is immediately sealed to prevent absorption of moisture. This gives commercial 76 per cent. caustic (Na_2O) containing 24 per cent. caustic soda (NaOH). The caustic "bottom" from the pots are contaminated with Fe_2O_3 and is red or yellow colour. It is re-dissolved and Fe_2O_3 separated by settling, the clear liquor being returned to the concentrating tank for further concentration.

CAUSTIC POTASH.

Caustic potash is largely used in the manufacture of soft soap. It may be prepared by decomposing a dilute solution of potassium carbonate with slaked lime. For this purpose one part by weight of potassium carbonate is dissolved in 12 parts of water, the solution placed in an iron or silver vessel provided with a lid, heated to boiling point, and then milk of lime gradually added until a portion of the filtered liquid evolves no carbon dioxide when treated with an acid. The solution is allowed to settle, and the clear liquid drawn off into a well-stoppered vessel. This is then evaporated in a silver basin until the hydroxide begins to volatilise. In order to ensure complete separation of the carbonic acid from the potash, not less water than that mentioned must be used, and the water which evaporates from time to time must be renewed, for when only four parts of water are present to one part of potassium carbonate no decomposition takes place. A concentrated solution of caustic potash is found

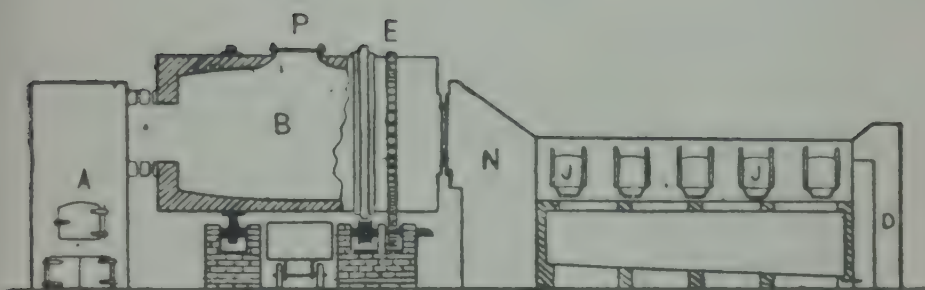


FIG. 21. ROTATING FURNACE.

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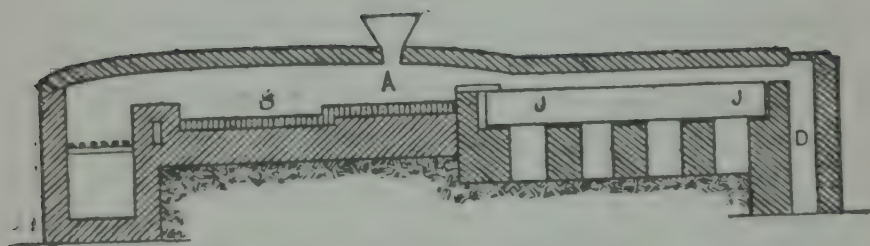


FIG. 22. BLACK ASH FURNACE.

[Page 189.

compose carbonate of calcium. A certain portion of the caustic potash of commerce is prepared in this way. It is usually cast in the form of all the impurities of the original potassium carbonate. It may be purified by dissolving in alcohol, and evaporating the clear solution to dryness in a silver basin.

Pure caustic potash may also be obtained by adding powdered potassium sulphate to a hot concentrated solution of barium hydroxide (baryta water) until a small quantity of sulphate of potassium remains in excess; this is then removed by a careful addition of baryta water; the clear solution is poured off from the barium sulphate precipitated in a silver basin, any baryta which remains in solution being deposited as carbonate by combination with the carbonic acid of the air.

SODIUM CARBONATE.

Common salt is placed in an iron pan upon the hearth of a reverberatory furnace and mixed with an equal weight of sulphuric acid; this converts it into sodium bisulphate, hydrochloric acid gas being given off. The latter is condensed by contact with water. The flame of the furnace is allowed to play upon the mixture of salt and sulphuric acid until it has become dry. The residue is then called 'salt-cake.' This is now broken up, mixed with an equal weight of lime-stone, and rather more than half its weight of small coal. The mixture is again heated upon the hearth of a reverberatory furnace. Carbonic oxide gas is given off and a residue is formed, consisting of sodium carbonate, lime, and calcium sulphide; this residue is called 'black ash.'

The 'black ash' is then treated with water, which dissolves out the sodium carbonate, leaving the calcium sul-

phide and lime behind. Any sodium sulphide that have formed is oxidised by blowing air through the liquid. The solution is finally evaporated to dryness, ordinary 'soda ash' being thus obtained.

PURIFICATION.

Soda ash contains as impurities common salt, sodium sulphate, and caustic soda, the last being formed by the action of the lime upon the sodium carbonate, and must be purified. The crude 'soda ash' is mixed with steam coal or sawdust, and again heated. Carbonic anhydride is given off, and this converts the caustic soda into sodium carbonate, and eliminates the other impurities. The mass is then lixiviated with water and the solution evaporated when oblique rhombic prisms of common 'washing soda' containing 10 molecules of water of crystallisation, separate out. The hydrochloric acid obtained as a by-product is used in the preparation of bleaching powder.

AMMONIA SODA PROCESS.

The manufacture of this is now a days carried out by the ammonia soda process as it possesses many advantages over the former Leblanc process.

RAW MATERIALS.

The raw materials required are common salt, limestone, ammonia and fuel. Common salt generally used in this process is the salt obtained from sea water. Of course this is purified and freed from iron, magnesium salts, etc. so as to produce pure brine solution.

Limestone is used for the manufacture of caustic lime and carbon dioxide. These are obtained by heating limestone in heaps with coke in kilns.

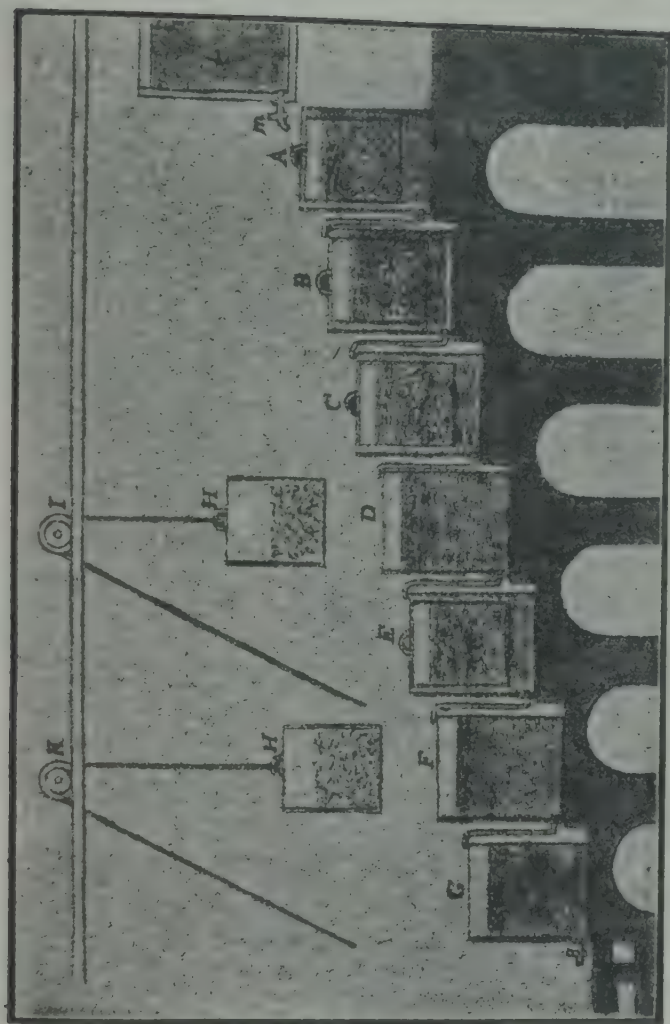
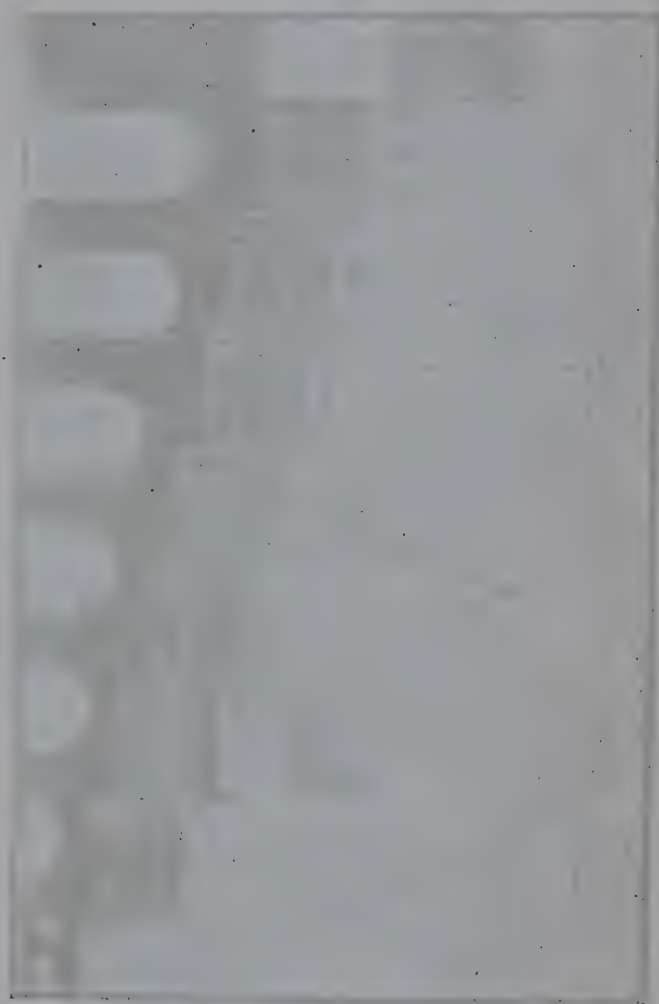


FIG. 23. LIXIVIATION OF BLACK ASH.

A-G—Vats.

L—Feeding Tank.

H—Perforated sheet iron vessels containing black ash.



PREPARATION OF BRINE SOLUTION.

The brine solution is prepared in the same manner as described under the Electrolytic process of manufacturing caustic soda. (p. 184.)

Next ammonia gas is introduced into the brine. Then only then is carbon dioxide gas passed into to make carbonate in solution. Carbon dioxide may be produced by the decomposition of lime in the manufacture of caustic soda. The introduction of ammonia gas into brine serves to impart only the necessary concentration of ammonia to also to purify the brine, a step very essential to the attainment of the degree of purity so highly valued in ammonia-ash.

This step is carried out in an ammonia absorbing apparatus, where saturated brine coming from different ammonia washes flows down from the top over a number of distribution plates consisting of mushrooms and division plates, while ammonia gas enters at the bottom and bubbles up through the down coming brine with vacuum assisting the gases through. These ammonia gases come from the ammonia still or distiller and pass through heat exchangers or coolers in which feed liquor is preheated, and then through partial condensers in which water is used as the cooling medium, the purpose being to condense steam from ammonia gases by partial condensation.

This distillation operation is essential and takes place with ammonium chloride and milk of lime. It is the same operation that is used in the total recovery of ammonia from by-product coke plants.

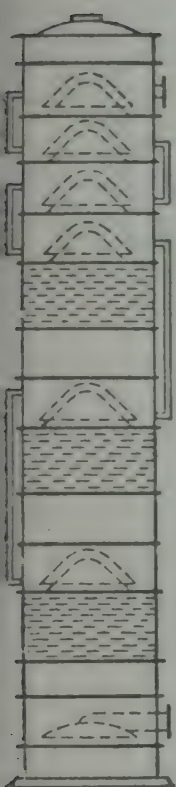
The brine that has taken up the necessary amount of ammonia is allowed to settle in large vats in series and the clear liquor from the final overflow, after passing through

the final coolers is pumped to the tower house for making sodium bicarbonate.

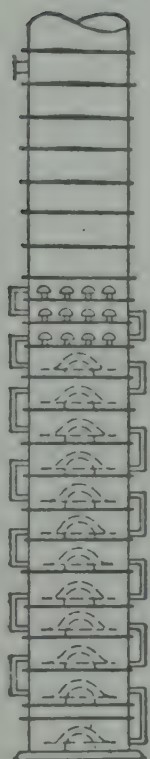
Chemically, the ammoniation of brine is very simple; mechanically, it is attended with many difficulties. The system must be tight and under vacuum. The gradual flow of brine must not be interfered with by the vacuum or suspension of brine flow would result. Separation of solids or muds in the apparatus and around the overhead pipes tends to plug the brine passage. To avoid this interruption a duplicate set of units and piping system must be provided for cleaning after a certain interval.

Ammonia absorption is a function of temperature. Unfortunately, considerable heat is developed during ammonia absorption and from condensation of steam. If the temperature is allowed to rise excessively, the vapour pressure of ammonia is increased and much ammonia will be driven out and passed on to the top creating a condition of hot-top in the absorber system.

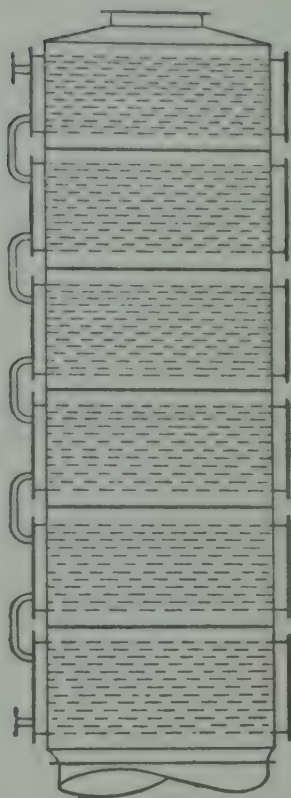
The temperature of the exit gas from the absorber at the top, entering the washer, should not be permitted to rise much above, 35°C . Hence cooling is very essential for ammonia absorption. In practice, methods of cooling both the liquor and the gas are employed at points most suitable. Unfortunately, neither of these methods of cooling is very satisfactory. Gas cooling is not efficient especially as crystals of ammonium salts are likely to adhere to the cooling tubes, and sulphide scale is formed on the metal surface in contact with the gas. If proper attention is given and the temperature gets too low, blocking up of the whole cooling section may occur from the formation of ammonium carbonate, and ammonium bicarbonate crystals.



PARTIAL
CONDENSER.



AMMONIA
STILL.



AMMONIA
ABSORPTION
APPARATUS.

FIG. 24. AMMONIA—SODA PROCESS.



ALPHABET



10
11
12

1000

To avoid troublesome mud formation in the absorber, tanks and cooler system, it has become a practice to pretreat the brine before it is sent to the system. This is done by the use of reagents, soda ash and lime, in the cold, or by magnesium. This pretreatment of brine solution is often necessary to minimise the trouble and renders the operation of the absorber system very efficient and smooth.

After the brine is saturated with ammonia, it is necessary to saturate it with carbon dioxide. The operation is pretreatment with ammonia to remove calcium and is carried out in a column.

ABSORPTION TOWER.

After settling and cooling, the ammoniated brine is pumped to the carbonating tower as shown in the diagram. The ammoniated brine enters near the top and the carbon dioxide gas is forced at the bottom, counter-currently. The bicarbonate suspension is tapped from the bottom, it is piped up to about 40 per cent. from the base, where tanks are located, and the suspension is filtered.

CONCENTRATION OF REACTANTS IN TOWER.

The reaction taking place in the tower is reversible. The yield of sodium bicarbonate and ammonium chloride is obviously dependent on the mass action effect, so it is important to keep the concentration of the reactions as high as possible. Unfortunately, in the process of ammoniation, increase in volume of brine, due to ammonia absorption and to admixture of steam condensate, lowers the sodium chloride concentration in the resulting ammoniated brine so that it is less than 94 per cent. of the theoretical saturation. The addition of solid salt after ammoniation, to bring the resulting ammoniated brine to full saturation,

ration with respect to sodium chloride is not practicable due to mechanical difficulties.

The next factor is the concentration of carbon dioxide in the gas. Efforts are made in ammonia soda plants to maintain the richness of both the dryer and kiln gases.

The third factor is the concentration of ammonia. It is comparatively easy to increase the concentration of ammonia as the resulting ammoniated brine contains on an average 15 per cent. ammonia by weight. But unless ample cooling area is provided in the absorber, any attempt to increase ammonia litre entails corresponding decrease in chlorine litre in the resulting ammoniated brine.

EFFECT OF TEMPERATURE ON THE REACTION.

The fourth factor which is even more far-reaching than its effect is the temperature, gradient in the column. Temperature has a direct bearing on the cooling capacity of the coils, on the temperature of green liquor in the feed, and on the temperature of carbon dioxide gases from the compressor.

FILTRATION OF SODIUM BICARBONATE.

The draw liquor from the columns is next filtered. The bicarbonate crystals belong to the monoclinic system but the crystals are so fine that they are seen with a microscope only as rodlike irregular particles. The filtration is generally performed with centrifugal machines which give dryness of the sodium bicarbonate of 80 per cent. or less. This dryness, however, is not measured by its moisture content, but by the amount of soda ash it yields. This per cent. of soda ash is called the yield of bicarbonate in plant parlance. Pure, dry sodium bicarbonate would have a yield of 63 per cent.

DECOMPOSITION OF BICARBONATE INTO SODA ASH.

The bicarbonate from the filters is next calcined to soda ash. The calcining operation is attended with many mechanical difficulties. The impurities such as ammonium bicarbonate, ammonium carbonate, ammonium chloride may be driven out with the moisture, but the last traces of carbon dioxide may be driven out with some difficulty. For the purpose it is necessary to control the temperature of the outgoing soda ash at the discharge end of the dryer. It is found that at above 160°C the ash might be free of bicarbonate but 180°C is a more conservative figure to insure complete decomposition of the bicarbonate in the ash. In order to carry out the operation the bicarbonate from the filters drops into a belt conveyor system, is fed to each dryer through a feed table, and, after calcining, comes out as soda ash at the extract end. It is then packed. This is known as 50 per cent ash and called light ash.

RECOVERY OF AMMONIA.

Ammonia is a comparatively expensive material, hence some equipment must be added to the plant whereby the ammonia gas may be recovered after the final reactions.

POTASSIUM CITRAS.

Potassium citras is a crystallisable substance much used in medicine. It is usually prepared by neutralising a saturated solution of potassium bicarbonate with a saturated solution of citric acid. The potassium of the bicarbonate unites with the citric acid to form the potassium citrate, and the carbon dioxide gas escapes, producing effervescence.

The resulting solution is directed to be evaporated dryness. The mass is again dissolved in the least quantity of water and set aside to crystallise.

Potassium citrate is principally used to increase quantity of urine and render it alkaline. It is employed in the treatment of acute nephritis and as a useful expectorant in the early stages of bronchitis.

POTASSIUM CHROMATE.

The source of this salt is chrome ore, a naturally occurring octahedral chromate of iron, found in various parts of Mysore, Baluchistan, and Singbhum.

The ore is ground to powder in a mill, and mixed with a quantity of coarsely powdered nitre. The quantity of nitre added should be less than that of the oxide of chromium which the ore contains. This mixture is powerfully heated, if possible, on the hearth of a reverberatory furnace for several hours in an iron pot during which time it is frequently stirred up with hot water when a yellow coloured solution is obtained. The solution is then evaporated briskly over a fire when the chromate of potassium falls down in the form of granular yellow solid. This is removed from time to time with a perforated ladle and collected in a wooden vessel with perforated bottom to drain away the solution. In this state it forms potassium chromate, which may be obtained pure by dissolving the salt in a small quantity of water and recrystallising. It is used by dyers, bleachers and tanners.

II.

The yellow, neutral salt, potassium chromate (K_2CrO_4) is prepared by heating chrome iron ore, previously pulverised and elutriated, with potassium carbonate.

and nitrate on the hearth of a reverberatory furnace. The oxygen of the saltpetre causes the higher oxidation of ferrous oxide and chromium sesquioxide, the latter being converted into chromic acid. The thoroughly sintered, not molten, mass is, after cooling, again ground up and lixiviated with boiling water, and also boiled for a time to extract the neutral potassium chromate. Wood vinegar is added to the solution to precipitate the alumina and silica, after which the clear liquid is evaporated, until a film of saline material begins to form, when it is left to crystallise. The crystals take a column-like form, and are of a lemon-yellow colour, readily soluble in water, but insoluble in alcohol, and have a great tendency to become converted into potassium bichromate. This conversion of the neutral salt into the bi-or acid-salt is at once effected by the addition to its solution of sulphuric or nitric acid, preferably the latter, on account of the formation of potassium nitrate, which may be used in the manufacture of neutral chromate. The potassium dichromate or acid chromate crystallises in anhydrous red coloured crystals, soluble in 10 parts of water.

POTASSIUM BICHROMATE.

I.

To a concentrated solution of yellow chromate of potassium, acetic acid is added in quantity equal to one half that required for the entire decomposition of the salt: the liquid is then concentrated by evaporation and slowly cooled, so that crystals may form.

II.

Chrome ore is first finely ground and sifted. It is then mixed with chalk; the mixture is spread in a thin layer on

the hearth of a reverbatory furnace, and heated to bright redness, with repeated stirring, for about 10 hours. The yellowish-green product consists essentially of neutral chromate of calcium mixed with ferric oxide. Having been ground and stirred up with hot water, sulphuric acid is added till a slight acid reaction becomes apparent, a sign that the neutral chromate has been converted into bichromate. Chalk is now stirred in to precipitate the ferric sulphate, and after a while the clear solution is run off into another vessel where it is treated with carbonate of potassium, which precipitates the lime, and leaves bichromate of potassium in solution. The solution is then evaporated to the crystallising point.

This process, when carried out on a large scale, is very economical.

III.

Jacquelain proposes that the chrome-iron should be mixed with chalk and the mixture heated and frequently stirred, then cooled, pulverised, and put into water, with the addition of enough sulphuric acid to produce a weak reaction, the result being the formation, first the calcium chromate, which, by the addition of the acid, becomes the bichromate of that base. The ferrous sulphate present in this solution is precipitated by means of chalk. In order to convert the calcium bichromate into the corresponding potassium salt, it is only necessary to add a solution of potassium carbonate, the result being of course the precipitation of calcium carbonate and the exchange of the chromic acid from the lime to the potassa.

IV.

According to Tilghman's process chrome-iron ore is mixed with 2 parts of lime, 2 of potassium sulphate and

heated for 18 to 20 hours in a reverberatory furnace. The fused mass is then taken out of the furnace and cooled. The solid thus obtained is reduced to pieces and lixiviated in the manner already described to produce the crystals.

V.

The chrome ore is roasted, ground in a mill, and passed through a sieve of 60 meshes to the inch. Caustic-potash lye is prepared by making 7 cwts of CaO in a solution of $\frac{3}{4}$ p.c. (potash carbonate) K_2CO_3 dried, ignited and powdered. Then mix with $4\frac{1}{2}$ cwts. of the ore and spread in a layer 2 inches deep upon a tray, over fire. The heat is maintained at bright redness, and the mixture turned over every 15 minutes; in about $\frac{4}{5}$ hours the operation is completed, when the mass is greenish-yellow. It is broken up to coarse powder and lixiviated in wooden pans, placed step like one above another, with a hot solution K_2SO_4 , (potash sulphate) which converts the calcium chromate into potassium chromate with precipitation of calcium sulphate. The liquid is allowed to run from one vat to another, until at last a saturated solution of potassium chromate is produced. This is run into a lead-lined vat and treated with sufficient sulphuric acid and water to convert the normal salt in the dichromate and the solution cooled.

SODIUM CHROMATE.

Sodium chromate is prepared as follows:—

6 parts of powdered chrome ore 44 p.c. are mixed with 3 parts of soda ash and 3 parts of chalk, and heated in charges of 1 ton in a reverberatory furnace for 8 hours. The operation is completed in about 4 hours, when the

mass is greenish-yellow. It is broken into coarse powder and lixiviated. The mass is lixiviated to produce a solution of 45°Be boiled down to 52°Be and allowed to crystallise in leaden pans. The crystals are first dried by a centrifugal machine, and finally heated to 30°C in a drying chamber, when they crumble to a yellow anhydrous powder containing 96 p.c. of the normal chromate.

For the production of dichromate, these crystals are dissolved to a solution of 40°Be and treated with sufficient sulphuric acid (chamber acid) to determine the conversion into the dichromate. the right point being found by potassium iodide and starch paper. Sufficient neutral sodium chromate is then added to bring the percentage of CrO_3 to 72.5. The liquor is cooled in lead tanks to 6°C , artificially if necessary, and the sodium sulphate crystallised out. The liquor is drained off, filtered if necessary, and evaporated to dryness in an iron pot with constant stirring. The residue is powdered while still hot.

SODIUM DICHROMATE.

Mix intimately 980 grams of lime, 960 grams of soda ash and 1000 grams of very finely powdered chromate. Convey the mixture to the floor of a reverberatory furnace and heat with the oxidising flame at a bright red heat to a period of 3 to 4 hours. The resulting mass, when cooled is pulverised and extracted with hot water until practically no more colour is shown in the wash water. The solution and washings are then evaporated to 35°Be . To this concentrated solution, sulphuric acid is added until the starch iodide paper test shows the presence of free chromic acid. The solution is then further concentrated until crystals of sodium sulphate separate. These are

removed by rapid filtration in the centrifugal machine and washed with a small quantity of water. The mother liquor and wash water from the sodium sulphate is then slowly evaporated with constant stirring. The crystals of sodium dichromate obtained are whizzed to remove adhering liquor.

Welberg mixes 6 parts of finely ground chrome ore, 3 parts soda-ash and 3 parts chalk in a reverberatory furnace in the oxidising flame; the change of the furnace being 1 ton. The hot mass is lixiviated with water, forming a lye of 84°Tw . It is then boiled down in an iron pan to 104°Tw ., and poured into tanks lined with lead. When cold, there are formed yellow crystals of sodium chromate. They are drained in a centrifugal machine, placed in a drying chamber, at a heat not exceeding 30°C and well ventilated. Here, they effloresce, and are converted into a yellow anhydrous powder.

For producing sodium dichromate, the chrome ore may be ignited with lime and soda, lixiviates, decomposes the neutral chromate with an acid, and evaporate to crystallisation.

CHAPTER XXII.

PHOSPHORUS AND PHOSPHATES.

PHOSPHORUS.

PHOSPHORUS is mainly manufactured from bone ash. For this purpose the bones of animals are calcined so as to destroy the animal matter that may adhere to them and are then reduced to powder.

Then put 1 cwt. (one hundred weight) of this fine ground bone ash into a stout earthenware tub and make into a thin paste with twice its weight of water. Then pour in a uniform but very slender stream 78 lbs. of concentrated sulphuric acid and stir all the while with a wooden rod. The heat thus excited in the dilution of the acid, and in its reaction upon the calcareous base, is favourable to the decomposition of the bone phosphate. Should the resulting sulphate of lime become lumpy, it must be reduced into a uniform paste by the addition of a little water from time to time. This mixture must be made out of doors, as under an open shed it is very injurious to health on account of the carbonic acid and other offensive gases which are extricated. At the end of 24 hours the paste may be thinned with water, and if convenient, heated, with careful stirring to complete the chemical change, in a square pan made of sheet-lead, simply folded up at the sides. Whenever the paste has lost its granular character, it is ready for transfer into a series of tall casks to be further diluted and settled. Thereby the clear super-phosphate of lime may be run off by a syphon.

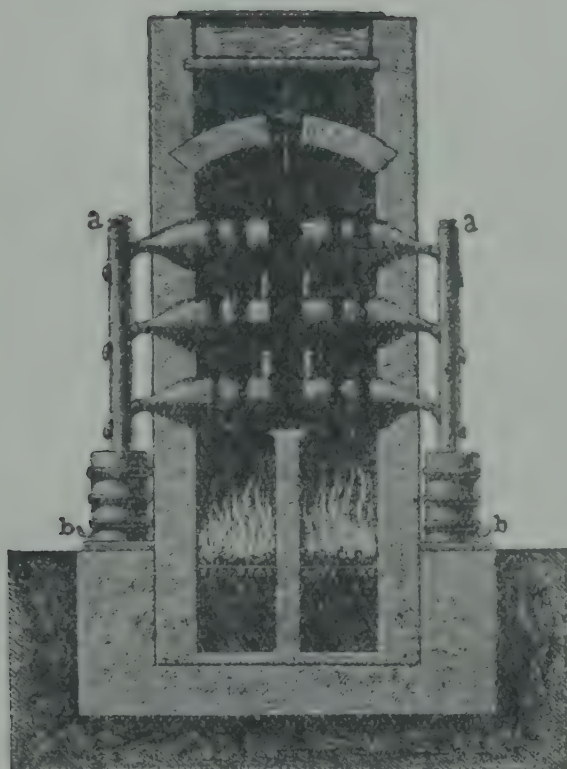


FIG. 25. PHOSPHORUS EXTRACTING PLANT.

from the deposit of gypsum. More water must then be added with the precipitate. When this subsides the supernatant liquor is again to be drawn off.

The collected liquors are then put into a leaden or preferably a copper pan, of proper dimensions, and concentrated by steady boiling, till the calcareous deposit becomes considerable. After the whole has been allowed to cool, the clear liquor is to be run off, the sediment removed, and thrown on a filter. The evaporation of the clear liquor is to be urged till it acquires the consistence of honey. Being now weighed, it should amount to 37 lbs. One-fourth of its weight of charcoal in fine powder, or about 9 lbs. is then to be incorporated with it, and the mixture is to be evaporated to dryness in a cast-iron pot. A good deal of sulphuric acid is disengaged along with the steam at first, from the reaction of the sulphuric acid upon the charcoal, and afterwards some sulphuretted hydrogen. When the mixture has become perfectly dry, as shown by the redness of the bottom of the pot, it is to be allowed to cool, and packed tight into stoneware vessels, fitted with close covers till it is to be subjected to distillation. For this purpose, earthen retorts of the best quality, and free from air-holes must be taken, and evenly coated over the surface with a compose of fire-clay and cow-dung. When the coating is dry and sound, the retort is to be two-thirds filled with the powder, and placed on proper supports in an air-furnace. Its fire is placed not immediately beneath the retort, but to one side, after the plan of a reverberatory, whereby the flame may play uniformly round the retort, and the fuel may be supplied when it is wanted, without admitting cold air to endanger its cracking. To the beak of the retort, properly inclined, one end of a bent copper-tube is to be tightly luted;

the other end of it is plunged not more than one quart of an inch beneath the surface of water contained in a small copper or tin-trough placed beneath, close to the side of the furnace. The heat of the furnace should be most slowly raised at first, but afterwards equally maintained in a state of bright ignition. The usual period of the operation on a big scale is from 24 to 30 hours. The phosphorus falls down in drops and concretes at the bottom of the water in the receiver. It requires to be purified by squeezing in a chamois leather bag, while immersed under the surface of warm water, contained in an earthen pan. The purified phosphorus is moulded in little cylinders, by melting it at the bottom of a deep jar filled with water, then plunging the wider end of a slightly tapering but straight glass tube into the water, sucking this up to the top of the glass, so as to warm it, next immersing the end in the liquid phosphorus and sucking up to any desired height. The tube being now shut at the bottom may be taken from the mouth and transferred into a pan of cold water to congeal the phosphorus, which is then pushed out with a stiff wire. The product is then cut to required size with scissors under-water and kept in bottles filled with water, closed with stoppers and stored in a dark place.

SUPERPHOSPHATE FROM MINERAL PHOSPHATES.

Phosphates occur in soil and rocks in the form of apatite. As a rule crystals of apatite occur in microscopic dimensions, but occasionally rich deposits of apatite crystals, several inches in length and 2 or 3 inches in diameter are come across. Such a deposit may be found in abundance in the district of Hazaribagh and is of considerable value to Indian agriculture. As this mineral

ard, it must be employed in the crushed state either by means of disintegrator or by means of *dhenki* provided with a block of granite at the base of the mortar. In pure apatite, apatite contains 90 to 92 per cent. of tricalcium phosphate.

Occasionally phosphates occur in rocks and soils in the form of phosphorite crystals without being contained with calcium chloride or fluoride.

Weavilite, which is hydrated aluminium phosphate, is another fairly common mineral but it has not been discovered in abundant quantity anywhere.

In the Nepal valley there is a kind of clay rich in phosphatic mineral.

Hard phosphatic nodules occur in fair abundance at Trichinopoly. These contain nearly 23 per cent. of phosphorus pentoxide and $12\frac{1}{2}$ per cent. of calcium carbonate. These nodules are very hard and as they contain much iron and alumina, they involve much waste of sulphuric acid converting it into superphosphate.

Nearly all the mineral phosphates actually mined are used for the manufacture of superphosphate. The mineral phosphate, having been finely ground, is treated with sulphuric acid, and is run into a den where the reaction is completed.

GENERAL PRINCIPLE OF MANUFACTURE.

Superphosphate is the name given to a soluble phosphate and can be prepared by treating insoluble rock or bone phosphate, with sulphuric acid. By the action of the acid, the insoluble tricalcium phosphate is converted into monocalcium phosphate, while in many cases some free

phosphoric acid is also formed. To prepare it on a large scale reduce the phosphate rock to fine powder in a ball mill and put in a cast-iron vessel provided with a stirring arrangement. Now pour the two-thirds of its weight of sulphuric acid of sp. gr. 1.6 and incorporate thoroughly. Now transfer the slimy mass into a brick-lined pit, where the reactions take place. The temperature rises to 110°C and much fume escapes. As the reactions progress, the charge stiffens and finally solidifies into a porous dry mass. In this way transfer several charges from the mixer into the pit until it is filled and then leave the whole for some days for the reactions to complete. Then dig out the product, pulverise it in a disintegrator and pack in bags.

MODERN METHOD OF MANUFACTURE.

The modern method of manufacture of this valuable substance comprises three principal operations; (1) Grinding the raw materials; (2) rendering the ground raw phosphate solution in sulphuric acid; (3) the drying of the superphosphate.

Raw phosphate should be carefully ground by means of ballmills, runners or flatstone mills; because it is found that the fineness of the phosphate contributes to a great extent to a perfectly successful superphosphate. Thus the powder should not leave more than 10 per cent. of residue on a 70 mesh sieve, and this residue should not exceed the size of groats; it is only at this state that all the phosphoric acid is rendered soluble. The ground material is then put into a mixing machine. It consists of an egg-shaped cast iron pan 64 inches wide at the top and 48 inches wide at the bottom, fitted with two discharge doors, with lever and counterpoise. This enables the mixing to be run into an enclosed space, called the

decomposition chamber sunk in the ground. In the pan a vertical shaft turns, driven by a cog-wheel gearing and carrying blades of a special form arranged in a helicoid manner, these lifts throw down, and triturate the mass and prevent it at the same time from being deposited and attached to the sides. It suffices to pull the bent leaves to open the discharge doors and let the liquid fall into the decomposition chamber.

Now to render the crushed raw phosphate soluble in sulphuric acid, the material is put into the mixer and the required amount of cold sulphuric acid of density between 10° and 55° Be. The machine is started at once. When proper mixing has been obtained, the mass is thrown down to the decomposition chamber by opening the doors.

Owing to the gas given off, the thick liquid effervesces; at the same time it heats up to 248° to 302° F. Gradually it settles in the den, and after an hour it sets. An addition of dolomite keeps it liquid for some time longer, so that the water evaporated is then much greater.

All the heat given off by the reaction ought to be utilised with that end in view, that is, carrying off the water. It is only when this is done that perfect solution is realised, and that a superphosphate that will behave well on subsequent manipulations is obtained.

BONE SUPERPHOSPHATE.

It has got a large use as a fertiliser. On an average raw bones contain 12 per cent. water, 28 per cent. nitrogenous organic matter, 10 per cent. fat, 44 per cent. calcium phosphate and 5 per cent. calcium carbonate. Large bones are again very slow in decomposition in the soil and

may be regarded as having no practical value. They are usually converted into bone superphosphate.

The first duty of the manufacturer is to bring all his care to bear on the storing of bones, because when they begin to rot they give off a bad smell. Besides, the decomposition of nitrogenous matter gives rise to a disengagement of ammonia, and there is a loss of nitrogen which may exceed $\frac{1}{2}$ per cent. The drying of fresh bones requires fastidious and costly manipulations; therefore, it is a good plan to sprinkle on them with water containing a small (0.5 p.c.) amount of carbolic acid or with spirits of turpentine.

EXTRACTION OF FAT.

The extraction of fat from bones is an indispensable operation, even when it is a question of merely converting the bones into dust, because the fat decomposes very slowly in the soil, and constitutes an obstacle to the phosphoric acid becoming soluble.

Fat may be extracted from bones by three processes:

- (1) By simply boiling with water in open pans.
- (2) By the action of steam in closed vessels.
- (3) By solvents.

EXTRACTION OF FAT BY WATER.

This process is the most ancient. It is carried out in a cylindrical cast-iron pan a little wider below than above. There is introduced a basket of perforated wrought iron containing the bones by means of a crane. The bottom of this basket can open into two semi-circular parts held by hinges on a cross bar. These two doors are closed by hooks, so as to receive the charge. The cast iron pan is fitted with a gutter so as to separate the fat

in the water in a continuous manner. The basket, being charged with bones in the fat extraction pan, water is run in to immerse the bones and steam caused to bubble from the bottom from a perforated steam coil. The water soon begins to boil causing the fat to rise from the bones through holes in the gutter at the same time as the excess water. The fat flows constantly from the gutter by the horizontal exit tube, whilst the water in the bottom issues through a bent tube without taking any fat with it. The removal of fat may be facilitated by a superficial push mounted on a vertical shaft fixed on the side of the pan. The bones are extracted in this way for an hour and a half after which they are removed from the basket to the washer. After washing, the bones are kept aside for drying; the same water may be used again and again until it is saturated with fat when it is replaced by fresh water. The water so obtained is utilised in the manufacture of glue.

EXTRACTION OF FAT BY STEAM.

This is done in large cast iron cylinders capable of containing 4 to 5 tons of crushed bones, the upper opening serving for the introduction of the bones, the lower opening for their discharge. These openings are closed by hinged lids as in an autoclave. Steam enters at the top and the fat runs off from the bottom by means of pipes situated near the aperture. Steam of from 2 to 4 atmospheres is used; for 1 to 2 hours the steam entrains the fat with it. The condensed water, charged with fat and phosphate, collects in the space reserved below the false bottom and is afterwards added in the manufacture of hydrogenised superphosphates, although the fat exercises an unfavourable influence of the dissolving of the phos-

phate. The solution of fat and gelatine is withdrawn from time to time, and the treatment by steam continued until a sample of the liquid contains no more fat. The bone thus devoid of fat is used in making bone dust.

EXTRACTION OF FAT BY SOLVENTS.

The process of extraction of fat by means of solvents, such as benzine, etc., is now employed in large factories. But as the process requires costly machinery which is beyond the means of average manufacturer we refrain from describing it here.

PREPARATION OF BONE DUST.

The fat extracted bones are now reduced to powder by means of ball mill or by a Carr's disintegrator. The powder yielded by the crusher is then passed through a No. 50 sieve. The core is returned to the crusher and finally reduced to the desired fineness.

CONVERSION OF BONE DUST TO SUPERPHOSPHATE.

The bone dust of required fineness obtained above is then mixed with the desired amount of dilute sulphuric acid. For this purpose a mixing machine is employed as already mentioned on page 206. It enables the mixing to be run into an enclosed space built on the ground floor or sunk in the ground; vertical shaft turns and triturates the mass and prevents it at the same time from being deposited and attached to the sides.

The work is easy and rapid. The pan is made of cast-iron, with 2 per cent. of a special alloy which renders it resistant to acid. The arms of the agitator and the blades as well as the valves are of cast-steel. The mixing shaft makes 60 turns a minute; the mixing is triturated (churn-

d) until the pulverized bone is intimately mixed with the acid. The acid contained in a lead-lined tank is drawn into a measuring tank by turning a valve. At the same time the crushed bone previously weighed is run into the mixer. The mixer works continuously; no stop is made except in case of a breakdown. When one mixing is finished the sides of the mixer are rapidly dusted with a little phosphate to neutralise any free acid left there which might corrode the metal. The charging of the mixer lasts $1\frac{1}{2}$ minutes; agitation takes 2 to 4 minutes; discharge takes half a minute. The decomposing chamber may be filled to $\frac{3}{4}$ ths of its height; the vacant space serves as a regulator for the evacuation of the gas. The decomposition of the phosphate by acid is effected not in the mixer, but principally in the chamber. Cold acid is used, and of density between 50° and 55°Be .

Owing to the gas given off, thick liquid effervesces, and forms air bubbles which rise to the surface: at the same time it heats up to 120° to 250°C . Gradually it settles in the chamber and after an hour it sets.

Then it is taken out and kept in heaps to dry. This generally takes place in about a month. The addition of a little nitrate of soda 1 to 2 per cent. considerably accelerates drying. But a rapid current of warm air is the most effectual in drying up the vitriolized bones. But before vitriolized bone is taken out, the obnoxious gas formed in the chamber is allowed to pass through a wash tower by means of fan and then let off in the air.

The superphosphate placed in a heap in the fresh state consolidates itself so much that it has to be broken down.

CHAPTER XXIII.

PIGMENT COLOURS.

PROCESSES of making some of the important pigment colours are given below:—

ULTRAMARINE BLUE.

Ultramarine is one of the most important blue pigments. It occurs in nature as the mineral lapis lazuli from which the pigment was formerly extracted by grinding and washing with water. It is now produced artificially on a very large scale, the annual output ranging from 10 to 15 thousand tons.

RAW MATERIALS.

The constituent elements of ultramarine are sodium, aluminium, silicon, sulphur, and oxygen. The pigment is prepared by a method which may be looked upon as the calcination of a mixture of an alumino-silicic acid and sodium sulphide. Raw materials are:—

- (1) Clay. Kaolin is generally used.
- (2) Silica. Kieselguhr is generally employed but sometimes finely powdered quartz is used.
- (3) Glauber's salt. Pure sodium sulphate free from iron is calcined and finally pulverised.
- (4) Sodium carbonate. The best commercial soda ash is calcined and finely powdered.
- (5) Sulphur. Roll sulphur free from non-volatile matter is used.

(6) Carbon. Coal and charcoal may be employed for the purpose.

VARIETIES.

There are three different varieties of ultramarine blue generally found in the market, namely—

(1) Sulphate ultramarine, the palest variety, which possesses feeble covering power.

(2) Soda ultramarine poor in sulphur, a pure blue variety, darker and possessing a greater covering power than the first.

(3) Soda ultramarine rich in sulphur and silica, the darkest variety.

COMPOSITION.

The first step in the manufacture of ultramarine consists in the powdering and mixing the ingredients. The most suitable proportions are as follows:—

	Pale.	Medium.	Dark.
Kaolin	100	100	100
Soda ash	9	100	103
Glauber's salt	120	—	—
Carbon or charcoal	25	12	4
Kieselguhr	—	—	16
Sulphur	16	60	117

If the clay employed differs in composition from china clay, the relative proportions of clay and silica must be suitably adjusted.

PROCESS OF MANUFACTURE.

After grinding the raw materials separately, they are incorporated according to the proportions as indi-

cated above and then submitted to roasting. This operation is carried out either by the direct or by the indirect process.

DIRECT PROCESS.

The direct or soda ash method yields blue ultramarine at one heating which may be done in muffles or in crucibles.

The required charge is put on the floor of the muffle to a depth 12 to 16 inches. A layer of firebricks is placed on the top of the charge and the front of the furnace is closed with loose bricks so that the samples may be taken out easily to determine the termination of the process. The process is very slow, requiring 3 or 4 weeks, of which 10 or 12 days are required for the slow cooling of the muffle. During all this time great care is necessary to exclude the air. The mass forms two layers, one bright blue, and the bottom greenish blue. These are separated, washed and levigated.

INDIRECT PROCESS.

In the indirect or sulphate method, the charge is put into crucibles, lids of which are then filled air-tight with a mortar of clay. The crucibles are then stacked in layers in a furnace and heated, slowly at first, eventually to a bright heat for about 2 hours. By this means air is excluded from the mass.

After the reaction is complete, the furnace is allowed to cool very slowly. When cold, the crucibles are opened and the green product is removed and powdered, constituting the ultramarine green of commerce. Now to obtain the more important derivative namely the blue pigment, this green substance is roasted with sulphur. The process

carried out in iron or fire-clay retorts, either by introducing the green ultramarine, together with the requisite amount of sulphur into a retort and raking the mass over intervals until the sulphur has burnt away, or by heating the substance and gradually adding the sulphur, each portion of which must be allowed to be burnt away before the next is added. The amount of sulphur taken in the conversion depends on the nature of the product to be derived. About seven per cent. of sulphur is required to convert the soda green and ten per cent. of the Glauber salt green into blue pigment.

LIXIVIATION.

The crude ultramarine blue is now submitted to lixiviating process. The filtering boxes employed for this purpose are made of hardwood 5-7 ft. long and 40-60 inches wide. About 6 or 8 inches above the solid bottom a false bottom is mounted, perforated with many $\frac{3}{4}$ -inch holes, and covered with string cotton filtering cloth. The cold, calcined ultramarine blue is mixed with a small quantity of hot water (75° - 80°C) in a vat, thoroughly mixed and transferred to a filtering box. In this manner all the numerous filtering boxes are charged. The clear filtrates are mixed and if sufficiently concentrated (15°Bé or more) the liquid is run off in crystallising tanks for the recovery of sodium sulphate. Weaker solutions, and the first two or three washings, are concentrated by utilising waste heat from the furnace. The ultramarine is washed with hot water until quite free from soluble sulphate, of which the crude blue contains about 15 per cent. It is then ground out in upright mills between hard stones until the requisite fineness is obtained. During this operation sodium silicate passes into solution, and it is therefore

necessary to use soft water for the grinding. The whole is then run into a large wooden vat and allowed to settle for 36-48 hours.

LEVIGATION.

The top blue liquor is siphoned off into another vat and left until the extremely finely divided particles of colour have settled; the product is afterwards added to the other preparations. The paste remaining in the large vat is distributed in quantities of about 2 cwt. into levigating tanks, three-fourths filled with soft water, and the colour equally distributed throughout the water. The larger particles settle rapidly, and after 2 hours' standing the liquids are run into other tanks. The next deposition of ultramarine takes 5 or 6 hours; the liquid is then siphoned into other tanks and a further settling of colour for 12 hours is allowed. The liquid that is now taken off contains extremely finely divided particles; they are precipitated in fourth series of tanks by the addition of alum, dilute mineral acid, milk of lime or other saline solutions, and the resulting blue paste is pressed. Passing from the first to the fourth series of tanks, the ultramarine becomes successively lighter, finer, bluer, and stronger. The different grades of product are then dried in sheds exposed to air.

The product dries in hard lumps, which must be powdered and sifted; for this purpose ball mills fitted with a continuous sifting device may be employed with advantage. Very fine sands of ultramarine are sifted in centrifugal sifters. It then remains to mix together the various shades and sorts in order to produce the standards of sale; this part of the work is of great importance, as the tinctorial power, fineness of division, depth and purity of colour in each standard, have to be exactly reproduced in bulk.

ADULTERATION.

In making cheaper brands of ultramarine blue, the pure material is mixed with 10 to 50 per cent. of gypsum. The latter has an extremely bad effect upon the brightness of certain kinds of ultramarine, which is minimised by incorporating a little glycerol or vaseline into the mixture.

PRUSSIAN BLUE.

Chemically this substance is an iron ferro-cyanide. A distinct variety of this substance is known as Paris blue. Three different kinds of Berlin blue are known, *i.e.*, neutral, basic, and a mixture of the two, differing in composition and prepared by different processes.

Neutral Berlin blue, also known as Paris blue, is obtained by pouring a solution of yellow prussiate of potash into a solution of iron chloride; the result is the formation of a large quantity of a magnificently blue coloured precipitate, very difficult to wash out and always retaining a certain quantity of the yellow prussiate, which cannot be removed by washing.

Basic Berlin blue is obtained by precipitating a solution of yellow prussiate with a solution of ferrous sulphate, the result being at first the formation of a white precipitate of ferrous cyanide. This gradually turns blue on exposure to air, because a portion of iron is oxidised and another portion takes up the cyanogen thus liberated, counteracting some of the ferrous cyanide into the corresponding ferric salt, which in its turn combines with the attached protocyanide to form Berlin blue. Basic Berlin blue is distinguished from neutral Berlin blue by being soluble in water; but this solubility is due to the presence

of some of the yellow prussiate, and is not a property inherent in the basic Berlin blue in a pure state.

As the materials employed on a large scale are neither pure ferrous nor pure ferric salts, the precipitate obtained consists at first of a mixture of neutral Berlin blue with more or less of the white ferrous cyanide, which afterwards becomes basic Berlin blue. Accordingly the Berlin blue of commerce is a variable mixture of neutral and basic Berlin blues.

PROCESS OF MANUFACTURE.

Ferrous sulphate and alum in equal quantities are dissolved together in boiling rain or river water; the fluid, while yet hot, is decanted from any sediment and forthwith poured into a hot aqueous solution of ferrocyanide, care being taken to stir the mixture, and to add the ferrous sulphate and alum solution as long as any precipitate is formed. The liquor is run off, and the precipitate washed with fresh water, until all the potassium sulphate is removed; after this the precipitate is drained on filters made of coarse canvas. This having been accomplished, the substance is suspended in water in a boiler, and, while being heated to the boiling point, nitric acid is added; after a few minutes' boiling, the contents of the boiler are poured into a large wooden tub or cask, and strong sulphuric acid is added. The solution is now allowed to stand for some time, during which the blue colour fully develops. The Berlin blue is then thoroughly washed with water, drained on coarse canvas filters, next dried, pressed, and cut into cakes; finally it is dried in rooms heated to 80°C . As Berlin blue, when once quite dry, is reduced to powder with great difficulty, and cannot be

brought to the state of fine division as when first precipitated, it is also present into the market in the state of paste. The alumina derived from the alum is so intimately mixed with the blue that the bulk of the mass is thereby increased without any very perceptible decrease in the intensity of the colour. If the quantity of alumina is very much increased, the colour, of course, becomes much lighter, and this variety of Berlin blue is then known as a general blue.

INDIGO CARMINE.

Indigo is an insoluble blue pigment, while the indigo carmine is soluble in water. Place in a porcelain or earthen pot 1 lb. of best indigo, finely pulverised, and add part each of fuming and ordinary sulphuric acid, and stir constantly to avoid too strong heating. Then cover the vessel and let it stand for 24 hours. When all the indigo has been dissolved, which may be recognised by a drop taken from the pot and thrown into a glassful of water, colouring the latter blue without forming a precipitate, pour the solution into water, dilute 18°Be , and precipitate the indigo carmine with carbonate of wash or soda; collect the precipitate upon a filter of wool or felt and let it drain off. This indigo carmine is extremely soluble in water but not in water containing salt. It is used in ink making.

CHAPTER XXIV.

ORGANIC COMPOUNDS.

CHLOROFORM.

CHLOROFORM is a very important product and is prepared by the action of chlorine on wood spirit in presence of an alkali. The operation is conducted in a still of a capacity triple that of the volume of the liquid to be employed, on account of the secondary reactions that occur, which cause the mass to swell up and froth. From 35 to 40 parts of water at 40°C in which 2' parts of quicklime, previously slaked, and 8 parts of bleaching powder are beaten up, are heated in a still on the water-bath. To these are afterwards added $1\frac{1}{2}$ parts of wood-spirit of 85 per cent. strength, and the temperature of the apparatus is increased rapidly until the still head is well heated, Gas is given off which emulsifies the mass and causes it to froth. When this occurs the heat is withdrawn, either by removing the fire from underneath the water-bath, or if heat is applied by a steam coil by turning off the steam. The distillation however is allowed to proceed without external aid. Towards the end of the operation, heat is again applied to terminate the reaction. The process is complete when the liquid which distils has no longer the sweet taste of chloroform.

The distilled product is a mixture of chloroform, methyl alcohol and water, and forms two layers in the receiver in which it is collected. The lower layer is chloroform, coloured slightly yellowish due to the

presence of a trace of chlorine gas. The liquid is decanted, washed with water to remove alcohol, and then with carbonate of potash solution. It is finally dehydrated with calcium chloride, then rectified over concentrated sulphuric acid, which is without action on chloroform, so as to remove the disagreeable odour due to a small quantity of a peculiar chlorinated compound. The water which floats on the chloroform in the condensation of the distilled products may be used again in the preparation of fresh chloroform.

In laboratory, chloroform is generally prepared by distilling acetate of potash and acetone in presence of freshly prepared bleaching powder.

ACETONE.

Acetone is produced in the dry distillation of acetates of lime and baryta. By heating acetate of lime to a certain temperature it decomposes into acetone and carbonate of lime; but besides the principal reaction, secondary products are formed by the decomposition of the salts of fatty acids, homologous with acetic acid. Moreover, as the acetate of lime often contains an excess of lime, the latter reacts on the acetate of lime to form marsh gas. Hence a portion of the acetone, which judged from the amount of acetic acid in the pyrolignite of lime ought to be obtained, is lost, in addition to the loss due to the decomposition of a portion of the acetone on the heated sides of the still. Care, therefore, should be taken to secure a uniform heat and regular but powerful agitation of the contents of the still. Theoretically, 100 lbs. of pyrolignite of lime containing 80 per cent. of acetate of lime, ought to yield 39 lbs. of acetone; but practically; even with the best plant only 25 lbs. is obtained which,

after rectification, yields only 20 lbs. of acetone per 100 lbs. of acetate of lime.

INSTALLATION OF AN ACETONE FACTORY.

As in the case of every industry in which condensers consisting of coils immersed in water are used, it is necessary to build the factory in proximity to as abundant a supply of water as possible. The reservoirs (storage tanks) for the different distilled and rectified products are installed in such a way as will avoid danger by fire. As previously mentioned, the manufacture of acetone consists in distilling acetate of lime in a retort at a temperature which reaches a dull red heat. Water is added to the crude acetone collected at the condenser to separate the oils which float on the top; it is then rectified, which yields pure acetone, methyl-ethyl acetone, and other acetone oils. The decomposition of acetate of lime is effected in cast-iron retorts fitted with an agitator. About 300 kilogrammes (600 lbs.) are distilled in one charge in these retorts.

Heating of the retort, was previously done in a bath of molten lead so as to secure a uniform heat. This had the defect of rapidly converting the lead into oxide of lead in contact with the air. Hence heating is now done by naked fire. To avoid overheating and at the same time to secure uniform heating, the hearth, with the fire bridge, is placed at a suitable distance from the bottom of the pan. This forms a rather large heating chamber, which avoids too great variations of temperature by irregular shaking. A dust chamber should be installed between the pan and the condenser to arrest the dust evolved, which might otherwise obstruct the condenser pipe. In small installations, the retorts are

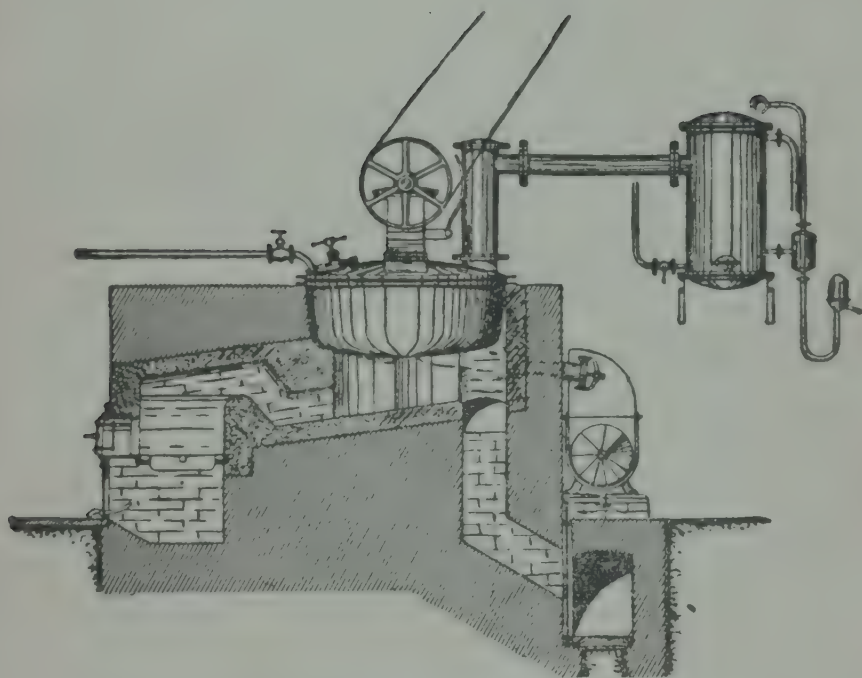


FIG. 26: ACETONE PLANT.

arged by emptying the sacks directly into the manhole. The pan is heated gently to a cherry red, then the acetate of lime is run in the manhole closed and the lid luted, after which the agitator is put in motion. The vapours which are first evolved are led to the chimney, because they consist in great part of water; after some minutes distillation ceases, which necessitates an increase in the heat, to commence the decomposition of the acetate and the actual distillation of the acetone. The vapours are then led to the condenser, consisting of rectilinear pipes, connected on the outside of the tank by elbows; this arrangement enables the coil to be easily cleaned, which is necessary since it always retains entrained dust which is not intercepted by the dust chamber. The condensed liquid has a more or less brown colour, due to the hydrocarbons which it contains and to entrainment of salts of lime in the form of dust. Towards the end of the distillation, the condensed product issues drop by drop. When this occurs steam is injected into the retort in order to dilute the remainder, so as to avoid the sudden inflammation of the gas contained in the still very hot retort when it is opened.

The residue of the above operation which is valueless in the form of a fine grey powder still possessing an empyreumatic odour. The crude acetone is collected in a cast-iron cylinder fitted with an agitator. It has an average density of 0.930 and contains 30 to 60 per cent. of pure acetone. Water is added until it contains only 10 per cent. of pure acetone, then slaked lime is run in, and the liquid is stirred for some time to neutralise the free acid, it is then allowed to settle, when the solution separates into two layers,—(1) A lower layer which is

a dilute solution of acetone; (2) an upper and darker layer (due to the tar that it contains), consisting principally of acetone oils, the major portion of the latter being thus separated from the aqueous layer. These liquids are run into different storage tanks. The acetone liquid is then distilled in a column still, taking care to separate the first runnings, which are slightly coloured and contain aldehydes, amines, etc., from the milky last runnings, which contain the higher acetones. Therefore collect the following: (1) The products which after the first runnings still contain oils and become turbid on addition of water; (2) those which mix in all proportions with water, yet decolorise permanganate in solution; and finally (3) most important as regards quality, products which give no reaction with permanganate of potash and are put on the market directly.

The portions which contain the oils are agitated with water once more so as to separate them. The solution contains a little acetate and is run into the crude acetone store tanks to be retreated. To purify the portion decolorising permanganate, the amount of this salt necessary for treating a given volume is determined in the cold state; then the corresponding weight of permanganate solution is added to the acetone, which is again rectified. In this distillation, which ought to be carried out with care, the portions of pure acetone, which pass between 56° and 58°C . (132.8° to 136.4°F), are collected apart for use in the manufacture of chloroform and iodoform. The acetone thus prepared contains 98 to 99 per cent.

Owing to the numerous applications of this product the acetone industry is at the present day of considerable

importance. Not only is an appreciable amount consumed in the denaturation of alcohol for industrial purposes but it is also used in the manufacture of celluloid and nitro-cellulose varnishes, chloroform and smokeless powders.

SULPHURIC ETHER.

150 grams. (80 c.c.) conc. sulphuric acid.

85 „ (110 c.c.) absolute alcohol.

A distilling flask ($1\frac{1}{2}$ litre) is fitted with a double-ported cork. Through one hole a thermometer is inserted, the bulb of which must be covered by the liquid in the flask and through the other a tap-funnel passes. The side-tube of the distilling flask is fixed by a cork into the upper end of a long condenser. An adapter is fitted at the lower end and passes through the neck of a flask, which is surrounded by ice. The apparatus is as shown in Fig. 1. The sulphuric acid and alcohol are cautiously mixed together in the distilling flask, which is then placed upon a sand-bath and attached to the condenser. The mixture is heated to 140° and alcohol runs in from the tap-funnel at the same speed as the liquid distils (about three drops a second). The temperature must be kept constant at $140\text{--}145^{\circ}$. When about twice the quantity of alcohol contained in the original mixture has been added and converted into ether, the distillation is stopped.

The receiver now contains, in addition to ether, alcohol water and sulphurous acid. The liquid is poured into a large separating funnel and a small quantity (10-40 c.c.) of dilute caustic soda is added and well shaken. After settling, the caustic soda solution is drawn off below, and about the same quantity of a strong solution of common salt is added, and the process of

shaking and drawing off repeated. The ether, which is now free from sulphurous acid and from most of the alcohol, still contains water. It is therefore poured into a large dry distilling flask and some pieces of solid calcium chloride added. It is allowed to stand loosely corked overnight. The distilling flask is now attached to a long condenser and heated on the water-bath.

PURIFICATION.

The ether, which distils, still contains traces of alcohol and water, which it obstinately retains and from which it can only be freed by a further treatment with metallic sodium. A few very thin slices of sodium are dropped into the receiver and the vessel closed with a cork, through which an open calcium chloride tube is inserted to allow hydrogen to escape and to prevent the entrance of moisture.

When the sodium produces no further action, the ether is decanted from the sodium residues into a distilling flask and distilled on the water-bath. A thermometer is placed in the neck of the flask to indicate the boiling-point which should be constant at 35° .

It must be remembered that ether is highly inflammable and also exceedingly volatile. Hence great care should be taken that no flame is in the neighbourhood of the liquid. It must on no account be distilled over the bare flame, but always over the water-bath, and then with a long well-cooled condenser.

METHYL NITRATE.

This ether is prepared by introducing 1 part of nitrate of potash into a retort, and dropping on to it a mixture of 2 parts of sulphuric acid and 1 part of methyl alcohol:

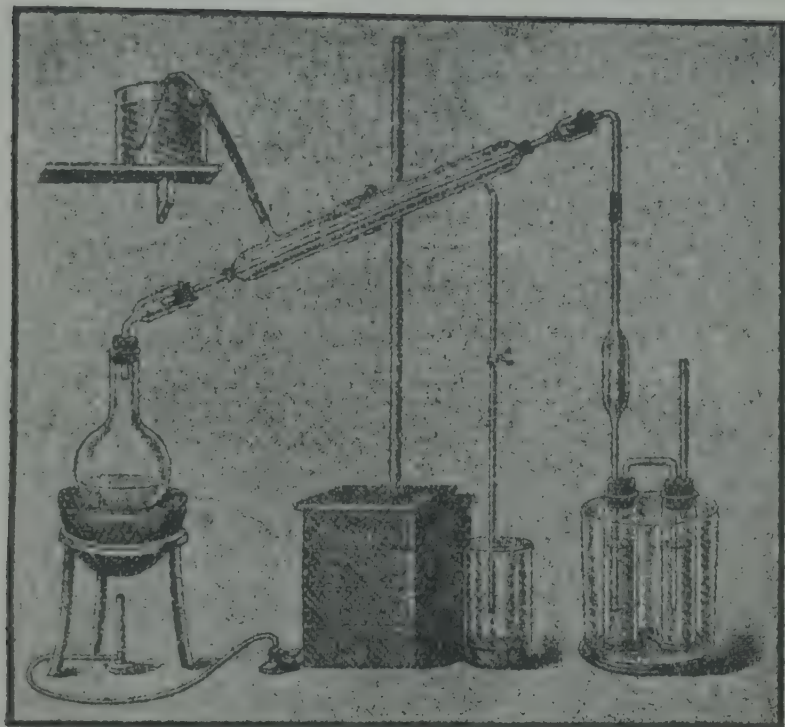


FIG. 27. ETHYL ACETATE DISTILLING APPARATUS.

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The reaction occurs spontaneously without the aid of heat. A very volatile liquid distils, and is led into a refrigerating condenser. The oily portion is afterwards washed with water, then rectified on the water-bath over a mixture of massicot (lead oxide) and chloride of calcium; the portion which passes over at 66°C is then collected. It is extensively used in the manufacture of methyl-aniline, one of the principal ingredients required in the ethyl-rosaniline colours.

ETHYL ACETATE.

Ethyl acetate is also known in commerce under the name of acetic ether. It is prepared by the action of acetic acid on alcohol, but as etherification of organic acid is accomplished slowly and incompletely, it is preferable to manufacture ethyl acetate by the intervention of a mineral acid like sulphuric acid, which is made to react on an acetate of soda and alcohol. Small quantities of sulphuric acid and alcohol, previously mixed, are run into a retort containing crystallised sodium acetate. Apply heat whereupon the liquid distils, and, after passing through a condenser, is collected in a receiver. The distilled product is agitated with twice its volume of water rendered slightly alkaline, it is then allowed to settle, and the ethyl acetate floating on the surface is decanted and passed over calcium chloride before being rectified. Since calcium chloride is soluble in acetic ether, bumping occurs in the still to such an extent as to render the operation a difficult one. It is therefore preferable to wash the crude product with a weak alkaline solution, and, after rectification, to agitate it with a saturated solution of common salt (sodium chloride), dry over carbonate of potash and finally rectify again. The wash waters, con-

taining dissolved acetic ether and alcohol are fractionally distilled; the liquid containing the acetic ether and alcohol is collected and used in a fresh operation.

Ethyl acetate possesses a very pleasant odour and is largely consumed in the preparation of artificial fruit essences. It is also used in medicine and in scenting vinegars.

AMYL ACETATE.

The preparation of this ether is carried out in the same way as that of ethyl acetate, using acetate of soda, sulphuric acid, and amyl alcohol. The rectified product is washed with water, then set aside to dry over calcium chloride, and rectified with a little lead oxide. It is advisable that the crude product be washed with acetic acid, diluted with its own weight of water, so as to remove traces of amyl alcohol which separates with difficulty; it is then washed with water, dried over chloride of calcium, and finally rectified over lead oxide. Amyl acetate is a colourless liquid, boiling at 125° ; its density is 0.876; it is insoluble in water, but soluble in alcohol and ether. Its aromatic ethereal odour, recalling that of the pear, has led to its use in confectionery for flavouring purposes. It likewise enters into the composition of some perfumes, imparting to them a pleasant odour, as well as into certain extra fine petroleum products for toilet use (petroles de luxe). It is also employed as a solvent for nitro-cellulose in the preparation of varnishes.

BENZALDEHYDE.

Few compounds have played so important a role in the development of synthetic organic chemistry as benzal-

aldehyde commonly known in commerce as oil of bitter almonds. To prepare the important substance take:—

50 grms. benzyl chloride.

40 „ copper nitrate.

500 c. c. water.

The mixture of benzyl chloride, copper nitrate and water is heated to boiling in a round flask ($1\frac{1}{2}$ litre) with a right condenser on the sand bath for a day (8-9 hours). A slow current of carbon dioxide is at the same time passed through the liquid to prevent oxidation of the benzaldehyde by absorption of oxygen from the air. During the process nitrous fumes are slowly evolved. When the reaction is complete, the contents of the flask are extracted with ether, and the yellow oil remaining after distilling off the ether, is well shaken with a saturated solution of sodium bisulphite and allowed to stand for some time. The colourless crystalline mass which separates is filtered, washed with a little alcohol and ether, and then drained on a porcelain filter. The aldehyde is regained by adding dilute sulphuric acid in excess and distilling with steam. The distillate is extracted with ether, dehydrated over calcium chloride, decanted and the ether distilled off. Yield is about 15 grams.

ACETALDEHYDE.

To prepare this take:—

(1) 100 grams potassium bichromate.

(2) 400 c.c. water.

(3) A mixture of 100 grms. (125 c.c.) absolute alcohol and 140 grms. (75 c.c.) conc. sulphuric acid.

(4) 100 c.c. methylated ether, which has been left to stand over solid caustic potash for a few hours, and then distilled off from the water-bath.

A round flask ($1\frac{1}{2}$ litre) is provided with a double-bored cork. A bent tube, which passes through one hole connects the flask with a condenser and receiver. A tap-funnel is inserted through the other hole. The flask is placed upon a sandbath, and the receiver is cooled in ice. It is important that all the corks should be tight, as a small leak will considerably diminish the yield. The potassium bichromate in small pieces and 420 c.c. of water are placed in the flask and gently warmed. The flame is then removed, and the mixture of alcohol and sulphuric acid, which may be used warm, is slowly added from the tap-funnel. The flask is occasionally shaken. A considerable rise of temperature occurs and the liquid darkens, whilst aldehyde, with a little water and alcohol, distils. When the mixture has all been added, the flask is heated on the sand-bath until all the aldehyde has distilled (about 150 c.c.). This may be determined by removing the cork from the flask and noticing if the smell of aldehyde is still perceptible. The distillate is now redistilled on the water-bath.

The flask is attached to an upright condenser in which the water is kept at a temperature of $30-35^{\circ}$. Alcohol and aqueous vapour condense in the condenser; the aldehyde, on the other hand, passes by a tube attached to a 100 c.c. pipette into two narrow (100 c.c.) cylinders, one-third filled with the dry ether, and cooled in ice-water. The aldehyde readily dissolves in the ether and is rapidly absorbed. If the ethereal solution is now saturated with dry ammonia gas, the whole of the aldehyde separates out in the form of colourless crystals of aldehyde-ammonia. The apparatus for preparing the dry ammonia is only a flask connected with a tower filled with soda-lime or quicklime. The flask containing strong ammonia

solution is heated by a small flame, when the gas is readily evolved and passes up the tower. The ethereal solution is saturated with the gas, and is then allowed to stand for an hour.

The ether is then decanted from the crystals which are drained at the filter-paper. Yield of aldehyde-ammonia is 25—30 grams. Pure aldehyde-ammonia, as follows: The crystals are dissolved in an equal weight of water and distilled on the water-bath with a mixture of $\frac{1}{2}$ parts of concentrated sulphuric acid and 2 parts of water, the receiver being well cooled in ice. The temperature of the water-bath is gradually raised until the water begins to boil, and the distillation is then interrupted. The distillate is dehydrated over an equal bulk of calcium chloride from which it is distilled in the water-bath, heated to 30° . The anhydrous aldehyde is kept in a well-stoppered bottle.

METHYL SALICYLATE.

The substance is otherwise known as the *oil of wintergreen* and is prepared thus:—

About 34 grams of salicylic acid should be placed in a round-bottomed flask having a capacity of at least 500 c.c. Then add 60 c.c. of methyl alcohol (prison) and slowly add with constant stirring 9 c.c. of concentrated sulphuric acid. To prevent bumping within the flask add a few pieces of porous tiling. Connect the distilling flask with a reflux condenser and heat on a steam-bath for $\frac{1}{2}$ hours. The oil of wintergreen formed usually collects at the bottom of the flask during the reaction. Distil off the methyl alcohol, transfer the residue to a separating funnel, add about 1000 c.c. of water, shake, separate the lower layer, which is the oil of wintergreen, the coveted

substance. Wash it in the separating funnel, first with water and then with dilute sodium carbonate solution to neutralise all traces of acid. The oil of wintergreen should then be separated from the water and purified by distillation. The oil will distil over at 224°C .

TERPINEOL.

Terpineol or oil of lilacs is a white oil having the odour of white lilacs. It can be prepared by simply distilling terpin hydrate with sulphuric acid and water. The amount of ingredients to be taken in this preparation may be determined by a few trials. The oil obtained in this manner is very concentrated and should be diluted with alcohol before using.

SODIUM SALICYLATE.

When preparing sodium salicylate it is necessary to ensure that the materials are perfectly pure and free from even traces of metals such as iron, and to work in porcelain, nickel, silver or glass-enamelled apparatus. $16\frac{1}{2}$ parts of pure salicylic acid and 10 parts of pure sodium bicarbonate are intimately mixed in a porcelain edge runner, with a little water, to a thick paste. It is advisable to grind the acid with the water and to add the bicarbonate in portions in order to prevent undue frothing. After most of the carbon dioxide has been evolved the mixture is evaporated to dryness in vacuo, at a temperature not exceeding 50° — 60°C . The dried sodium salicylate is powdered and sifted, or, if flaky crystals are required, is recrystallised from hot alcohol, with the addition of some ether.

Sodium salicylate is prescribed in acute rheumatism, for which it is specific, and is useful in influenza, diabetes,

iatrica; and acute tonsilitis. It is used as an antipyretic in pneumonia, typhoid fever, and all pyrexial affections. It is also an effective antiseptic for fermentative dyspepsia, and increases the acidity of the urine.

BENZOIC ACID.

Benzoic acid occurs naturally in benzoin and in the balsams of Peru and Tolu. It is prepared synthetically from toluene thus:—Rectified toluene is heated to 110°C , in an earthenware-lined or lead-lined cast-iron vessel and chlorine gas passing through lead pipes, is allowed to bubble through it until it possesses at 15°C , a specific gravity of 1.35. The product consists mainly of benzo-tri-chloride mixed with some benzalchloride. Iron must be carefully excluded from the apparatus, as ferric chloride acts as a catalyst and causes the chlorine to enter the nucleus, with formation of chlorotoluenes. It is necessary that both toluene and chlorine should be dry, for moisture also facilitates nucleus substitution. The evolving hydrochloric acid and volatilised toluene are condensed in earthenware condensers and washing towers.

Under the above conditions it is not necessary to employ a carrier for which phosphorous trichloride has been commended, or to conduct the chlorination in ultra-violet light, though the latter procedure is said to be advantageous in accelerating the reaction.

60 Kilos of benzotrichloride are added to 200 kilos milk of lime, containing 34 kilos of lime, and 20 grams iron powder, in a cast-iron vessel, fitted with stirring bar and connected to a condenser. The mixture is heated by direct steam to 50°C , at which point the temperature rises spontaneously; when the water and benzalde-

hyde commence to slow down, direct steam is again applied, and the benzaldehyde is distilled away.

The operation takes 9—10 hours. The residual liquid is filtered, transferred to a wooden vat fitted with a stirrer, and acidified with hydrochloric acid to precipitate the benzoic acid. This is filtered off after cooling and purified by recrystallisation from water, or by sublimation after drying.

CHLORAL HYDRATE.

Chloral hydrate is probably the best known hypnotic. It was first prepared by Liebig by the continuous chlorination of absolute alcohol.

The commercial preparation of chloral hydrate depends on the chlorination of absolute alcohol, a slow process which is carried out over a long period. Chlorine is slowly passed into absolute alcohol. Heat is formed at first, and the vessel must be cooled, but after a time the action becomes less violent, and heat is applied in order to raise the temperature first to 60°C , and finally to 95°C . The process, as thus carried out, takes from ten to fourteen days. The time may be reduced to three to five days by carefully designing the plant so as to obtain the most efficient absorption. A lead-lined jacketed vessel is used, fitted with a stirrer and numerous tubes for the distribution of the chlorine. Several vessels may be arranged in series, so that the excess of chlorine from the first passes to the second, and so on. When the liquid is completely soluble in water, the reaction is complete, and the liquid consisting of chloral alcoholate is transferred without cooling to an enamelled still, where an equal volume of sulphuric acid is slowly added. The mixture is then gently boiled under a reflux condenser until no more hydro-

Chloric acid is evolved. It is then fractionally distilled until the temperature of the vapour is 100°C . Ethyl chloride distils off first, followed by alcohol. Chloral distils at from 90° to 100°C . The crude chloral is redistilled over calcium carbonate. The chloral is converted into the hydrate by the slow addition of water. It is immediately spread on a plate, and solidifies. Chloral hydrate may be crystallised from benzene or chloroform.

ETHER.

The ether with which chemists are most familiar is diethyl ether, commonly called ether.

Fit up an apparatus like the one in Fig. 1. It consists of a distilling flask furnished with a tap-funnel and thermometer, the bulb of which is immersed in the liquid in the flask. The liquid consists of a mixture of 80 c.c. of concentrated sulphuric acid and 110 c.c. of concentrated sulphuric acid, and 110 c.c. of absolute alcohol. The flask is heated on a sand-tray, and kept at a temperature of 140° — 145°C , whilst fresh alcohol is allowed to drop slowly in from the tap-funnel. Ether and water collect in the receiver, which is cooled in ice or cold water. The distillate is purified by shaking it with a little dilute caustic soda to remove sulphurous acid, which is derived from a slight decomposition of the sulphuric acid. The caustic soda is drawn off, and a little strong solution of common salt added to dissolve out any alcohol which may be present. The salt solution is removed, and the ether is first dehydrated over solid calcium chloride and finally over metallic sodium. To carry out the process successfully thin slices of sodium is added to ether contained in the flask, which is kept cool by water. Effervescence begins and which it slackens more sodium is added until after a

few hours, the addition of fresh sodium produces no further action. Then the ether is distilled from the water-bath. The distillate is now free from water.

Ether is principally used as an anaesthetic, and notwithstanding the many efforts made to supplant it, it continues to be the best agent yet discovered for producing insensibility to pain in surgical operations. It is also used as a solvent.

Ether being inflammable and its vapour heavy, special care should be observed in pouring it from one vessel to another away from fire.

ETHYL BROMIDE.

Ethyl bromide is used as a local or general anaesthetic. It may be prepared thus:

Ten grams of red phosphorus and 70 c.c. of ethyl alcohol are placed in a distilling flask, attached to a condenser and receiver. The receiver is connected with a soda-lime tower. A tap-funnel containing 20 c.c. of bromine is fixed through a cork in the neck of the distilling-flask.

The flask is cooled in water and the bromine slowly added. The flask is then left for several hours, and the contents distilled from the water-bath. The sodalime tower absorbs any fumes of hydrochromic acid which are evolved.

The distillate consists of ethyl bromide, which is purified by shaking it with a little sodium carbonate solution in a tap-funnel to remove both alcohol (which dissolves in the water) and hydrobromic acid (which combines with the sodium carbonate). The lower, and therefore heavier insoluble, layer is the ethyl bromide, which is withdrawn and separated from the water. It still contains

little water, which is removed by adding a few pieces of solid calcium chloride (dehydrating agent), and then by redistilling the liquid.

Ethyl bromide may also be prepared by adding absolute alcohol to cold concentrated sulphuric acid. Sodium bromide is then added, and the temperature slowly raised until ethyl bromide begins to distil. The distillate is collected under water, and when no more comes over, sodium carbonate is added to the aqueous layer until it is slightly alkaline after shaking. The ethyl bromide is separated and washed first with water, then with a concentrated sulphuric acid. Finally it is redistilled.

FORMALDEHYDE.

Formaldehyde is usually prepared as a solution in water. Its solution is variously termed Formalin, Formal, Methanal and Liquor Formaldehyde. It is prepared technically by the oxidation of methyl alcohol, derived from wood spirit. The oxidation of methyl alcohol is carried out by passing its vapour mixed with air over a catalyst heated at about 450°C .

The conditions which require to be observed in order that good yields may be obtained have been worked out by Orloff. The methyl alcohol should be at least 90% in strength. It should contain not more than 1% of acetone. The highest conversion, employing a copper catalyst is obtained when for 1 part of methyl alcohol 0.39 part of oxygen is taken. The depth of the catalyst is of importance, when copper gauze 100 mesh is employed, 120 millimetres is found to be the best.

The catalytic chamber is the most important part of the apparatus for making formaldehyde. It consists of

169 copper tubes, 800 m.m. long, external diameter 19 m.m., thickness of wall 17 m.m., arranged in circles set in two copper plates. The whole is enclosed in a copper box, having on one side a tube through which the air and methyl alcohol mixture is introduced, on the other an exit for the formaldehyde-nitrogen vapour. Inside each tube is set one of glass, 300 m.m. long and internal diameter 14.75 m.m. Each glass tube contains a roll of copper 120 m.m. long, made of gauze of 15×15 meshes per square m.m. A device for igniting gases, in order to start the reaction, is provided and may consist of an electrically heated wire. A catalyst of this size consumes 170 kilos of methyl alcohol in 10 hours, affording 255 kilos of formaldehyde 38%.

Air is compressed by a pump into a reservoir. Methyl alcohol stored in an overhead tank flows down into the carburettor in which it is maintained at a constant level, and is warmed by means of a closed steam coil. Air is blown into it from the reservoir, through a perforated coil. The temperature then passes into the catalyst chamber in which, after being started by ignition, the reaction proceeds without further addition of heat. The temperature maintained in the catalyst chamber is 450°C . The issuing vapours pass into the fractionating column in which 38-40 % formaldehyde is condensed, the methyl alcohol passing over, together with the waste gases, into a condenser. In this is condensed the greater part of the excess of methyl alcohol which runs into a store tank from which it can be pumped up into the overhead storing tank. The gases, which still contain some methyl alcohol, pass into a gas scrubber in which they are washed with water. The washings are then fractionated in the fractionating column,

the methyl alcohol being condensed and run into the storage tank.

Commercial formaldehyde solution contains 35-40% of formaldehyde, and 10-15% of methyl alcohol. It is a powerful antiseptic, disinfectant and deodorant.

GLYCERINE.

Since the outbreak of the war the value of glycerine has risen enormously owing to its rapidly growing demands in manufacturing explosives and also in pharmaceutical purposes. This high demand has rendered its manufacture a matter of vital national importance.

Glycerine was first discovered by the Swedish Chemist Scheele in 1779 while saponifying olive oil with lye. But this process has now been entirely discarded. Following upon the results of Chevreul's investigations regarding the composition of fats that they are compounds of saturated or unsaturated fatty acid, with tri-hydric alcohol glycerol, soap and candle makers began to attack the problem of separating fatty acids and glycerine by saponification of fat.

There are however, various methods which are now adopted for the production of glycerine the simplest and the most widely used one still being that of the saponification of fats. Accordingly as the end in view is either soap or candle, caustic soda or milk of lime is used as the saponifying agent. Glycerine of commerce is now mostly derived thus.

It is to be noted that the glycerine water which is obtained in soap works is in a very dilute condition with enormous inorganic and organic impurities and hence the recovery of glycerine can only be carried out economically in very large installations. Therefore it does not encour-

age the small soap makers to recover glycerine from their waste lye. It is however customary in some parts of Europe where small soap factories are still in operation, not to deal with the recovery of glycerine but to send it elsewhere to be recovered in a Central Glycerine Works in the vicinity of the factory.

Fats may also be hydrolysed with superheated steam either alone or in presence of certain basic oxides, specially lime, magnesium or zinc oxides which exert a strong catalytic acceleration upon the rate of hydrolysis. Unfortunately, however, the hydrolysis by steam alone requires a high temperature (about 200° - 230° C.) before it proceeds at a technically useful speed. Hence it is commercially uneconomical. There is no doubt that certain advantages are gained in either way with respect to the elimination of the more costly chemical caustic soda and also in the production of relatively more concentrated lye. But the colour of the autoclave fatty acids is always somewhat damaged even at the comparatively low temperature of 150° C which is the lowest limit for splitting fat with steam under pressure.

Catalytic hydrolysis of fats is gradually finding favour in certain countries. When oleic acid is heated with sulphuric acid in presence of benzene or naphthalene a product is obtained, called the "Twitchell Reagent," which possesses the property of hydrolysing fat at boiling water temperature under normal pressure. As a matter of fact $\frac{1}{2}$ -1 per cent. of the reagent or any one of its various modifications now worked out by different chemists, is sufficient to split up 95 to 97 p.c. of total fats present, into their respective component acids and glycerine. The advantages of this process are its cheapness in reagent and in the consumption of steam, the glycerine

water yielded being of 10-15 p.c. strength. It has got the compensating disadvantages in the length of time (24 to 36 hours), required for hydrolysis and also in the tendency of producing dark coloured fatty acids.

Alike the preceding one, fats can be fermented into glycerine and acids in presence of water and hydrolytic enzyme lipase, which acts as a catalytic agent in this case. The enzyme lipase is widely distributed in nature and occurs in vegetable seeds, of which certain oil bearing varieties are specially rich in it. The operation can be performed at the normal shade temperature of a tropical country without the application of any elaborate machinery and manufactured chemicals. It yields glycerine water of higher strength (15 to 17 p.c.) than can be had by any other existing methods and the colour and quality of the resulting fatty acids are so excellent that they can with advantage be utilised for widely different purposes, as for instance, for soap or candle making, as edible fats and lubricating grease. As low grade fats are made use of in this process the quality of glycerine produced is often slightly inferior to one obtained by using autoclave.

RECOVERY OF CRUDE GLYCERINE.

The production of crude glycerine from any of the above types of lye consists essentially of two stages.

The first stage of the process involves the production of a neutral lye, alkali in soap-lyes being neutralized by mineral acid, and sulphuric acid when present in the other types being combined with lime or baryta, and the resulting salts removed from the system as precipitates as far as possible. Organic matter, whether albuminoid, mucilage, or fatty acids, is removed as far as possible by coagulation or precipitation with metallic compounds (usually

hydrated iron oxide or alumina) and the clarified neutral lye is then ready for concentration.

The second stage of the process is carried out in a double effect or triple effect multiple tube vacuum evaporator, the feed and rate of evaporation being arranged so that the liquor in the first pan does not reach the salting-out point. Salt, however, is precipitated in large quantities in the second pan, and this is collected in a salt box which can be periodically emptied as it fills up without breaking the vacuum on the pan. The final concentration of the glycerine can rarely be effected in a double-effect, the pan either working as a single effect pan or else the charge is run out and transferred to a separate single effect evaporator. Solid crystalline salts gradually fan to the base of the vessel and are drawn off into "salting boxes."

PURE GLYCERINE.

The product, which is variously known as "refined" "industrial" or "industrial white" glycerine, is obtained either by filtration of the crude one through layers of activated charcoal, by agitation with a small percentage of sodium hydrosulphite or sodium formaldehyde-sulphoxylate, or by similar means. This refined quality of crude glycerine is used in the ink and plastic trades, and also to some extent in the production of the transparent soaps and other purposes where distilled glycerine is not essential.

The crude glycerine is therefore submitted to distillation under reduced pressure in a current of superheated steam and the condensed glycerine is further concentrated to an almost anhydrous state by heating in vacuum-pans.

A single distillation of good crude glycerine on a commercial scale usually produces a distilled glycerine sufficiently pure for conversion into nitroglycerine or dynamite, although not absolutely colourless; this once-distilled glycerine is known in the trade as dynamite glycerine.

To obtain colourless glycerine which, except for the presence of about 2 per cent. of water, approximates the pure compound glycerol, $C_3H_5(OH)_3$, a second distillation (usually accompanied by refining with charcoal or similar means) is necessary; the twice-distilled glycerine, which is that used for medicine, pharmacy, and edible purposes, is known as chemically pure glycerine.

On a small scale, distillation may be carried out in a pot-still heated evenly by gas. The charge of crude glycerine is placed in a still, connected by a swan-neck to a condenser system and a current of super-heated steam allowed to flow evenly through the heated crude glycerine. The whole apparatus is evacuated by a pump. The refined glycerine with water vapour distils over and is condensed in a receiver.

This method entails considerable loss of glycerine by decomposition due to local overheating in the still, while the regulation of steam current is difficult and tends to excessive splashing and frothing.

This method is therefore now being replaced by modern methods of distillation devised by van Ruymbeke and Wood, which yield a greater amount and better quality of glycerine. The description of these methods is beyond the scope of the present book.

CHAPTER XXV.

MISCELLANEOUS CHEMICALS.

HYDROGEN PEROXIDE.

HYDROGEN peroxide forms an important ingredient in the preparation of certain mouthwashes. It is usually prepared from a cheaper peroxide, e.g., barium peroxide. The barium peroxide, finely powdered, is added gradually to a suitable dilute acid, e.g., hydrochloric acid. In this case the barium in solution is subsequently precipitated with sodium sulphate, so that after filtration a solution containing hydrogen peroxide and sodium chloride is obtained. If dilute sulphuric acid is employed instead of hydrochloric acid, after filtering off the insoluble barium sulphate, an aqueous solution of hydrogen peroxide is obtained, containing, however, some impurities derived from the barium peroxide.

PURE PEROXIDE.

In order to obtain a pure aqueous solution of hydrogen peroxide, the pure hydrated barium peroxide is prepared as follows:—

Commercial barium dioxide, very finely powdered, is brought little by little into dilute hydrochloric acid, until the acid is nearly neutralised. The cooled and filtered solution is then treated with baryta-water, in order to precipitate the ferric oxide, manganese oxide, alumina, and silica which are always present. As soon as a white precipitate of the hydrated barium dioxide makes its appearance, the solution is filtered and to the filtrate concen-

ated baryta-water is added; a crystalline precipitate then falls consisting of hydrated barium dioxide. This is well washed and preserved in the moist state in stoppered bottles. In order to prepare hydrogen dioxide by means of this substance, the moist precipitate is gradually added to a cold mixture of not less than five parts of water to one part of concentrated sulphuric acid, until the mixture remains very slightly acid. The precipitate of barium sulphate is allowed to settle, and the liquid filtered. The small trace of sulphuric acid which the filtrate contains can be precipitated by addition of dilute baryta solution.

A concentrated solution of hydrogen peroxide may be prepared by adding sodium peroxide to well-cooled diluted sulphuric acid (20 per cent. calculated amount). On standing, about two-thirds of the sodium sulphate crystallises and is separated by filtration. The filtrate is distilled under diminished pressure (Merck). Merck's "perhydrol"—the so-called 100 per cent. hydrogen peroxide—contains 30 per cent. peroxide, one volume of the solution yielding 100 volumes of oxygen. If a concentrated solution of hydrogen peroxide be distilled under diminished pressure, water distills over first, and subsequently nearly pure hydrogen peroxide (96 per cent.) distils over.

Hydrogen peroxide may also be manufactured by the hydrolysis of permono-sulphuric acid in the presence of sulphuric acid. The hydrogen peroxide may be obtained by distillation under reduced pressure or by extraction with a suitable solvent.

The concentration of hydrogen peroxide solutions may be ascertained (1) by titration with standard potassium permanganate in the presence of dilute sulphuric

acid; (2) by treatment with excess of potassium iodide solution and subsequent titration of the liberated iodine with standard thiosulphate.

A 3 per cent. solution of hydrogen peroxide on decomposition yields approximately ten times its own volume of oxygen (10 vol. peroxide).

ALUM.

At one time alum was relatively important industry in certain parts of India, but the importation of cheap alum and the easy distribution of this article from the railways has resulted in the practical extinction of the native industry in most localities. Among the most important places where alum used to be manufactured may be mentioned:—

Pulwaria in the Shahabad district in Bihar; Mourr in Cutch and Maki Nai in Sind; Khetri and Sinjhana in Jaipur State in Rajputana; and Kalabagh and Kotki in the Mianwali district in the Punjab. To-day the only locality in which alum is prepared on a commercial scale and from which returns are available is Kalabagh. (Records of the Geological Survey of India, Vol. LXIV. p. 314). In the Salt Range near Kalabagh, alum shales rich in sulphur are found in enormous quantities. These shales as they are brought out from the mines are subjected to the roasting process which being continuous may be carried out in the open.

ROASTING.

Alum is a double sulphate of potassium and alumina or of ammonia and alumina. The most important raw material for the manufacture of alum is bauxite, a mineral found abundantly in India.

Its chemical composition is K_2SO_4 , $Al_2(SO_4)_3 \cdot 24H_2O$ and $(NH_4)_2SO_4$, $Al_2(SO_4)_3 \cdot 24H_2O$.

CALCINING BAUXITE.

In the manufacture of alum, bauxite in lumps is first all calcined in a reverberatory furnace until it becomes friable, great care being taken that the heat be not sufficient to indurate it, which would destroy its subsequent solubility. It is next reduced to fine powder, sifted and introduced into the cast-iron boiler lined internally with lead and stoneware, which contains about 45% of its weight of sulphuric acid (sp. gr. 1.45).

CONVERSION OF BAUXITE TO SULPHATE.

On applying heat a violent action soon takes place and the pressure inside the boiler sometimes rises to 4 atmospheres. After ten or fifteen minutes the action is completed, and the pressure gradually sinks. By opening a valve the pressure is reduced to atmospheric, the manhole is opened, the pasty mass is diluted with water until a concentration of 29°Be is attained and the liquid mass run out into tall settling tanks. After four days the clear liquid is decanted off and evaporated until the concentration has reached 40°Be . The concentrated aluminium solution is now run into a large tank, where it is allowed to become quite cold.

The potassic or ammoniacal salt is now to be added. To make potash alum, either the neutral sulphate or the chloride of potassium can be used. In making ammonium alum, ammonium sulphate is used. This combines with the sulphate of aluminium dissolved in the liquor and forms the double sulphate, alum, which being only slightly soluble in cold water is thrown down in crystals.

Before adding potassium of ammonium salts a test is to be made to ascertain the exact percentage of sulphate of aluminium in the tank. Usually 174 parts by weight of potassium sulphate or 114 parts of ammonium sulphate will be required for 342 parts of aluminium sulphate. This is dissolved in the smallest possible quantity of hot water added gradually to the liquor in the tank, and two mixed up together by vigorous stirring. As soon as they have properly combined, the alum is deposited in small crystals all round the walls and bottom of the tank. After a day or two the mother liquor is drained off, the crystals are washed with as small a quantity of cold water as possible to remove any adhering impurities. Some alum is necessarily dissolved off at the same time, but that can be again recovered, so that it is not wasted. The alum crystals are again dissolved in hot water and crystallised therefrom, after first making a solution of sp. gr. 1.5.

ALUM FROM SHALES.

Practically all the alum which is produced in India is made by the separation of sulphate of alumina (bauxite) from decomposed pyritous shales, with the addition of nitre of wood ashes to provide the hydrated double sulphates of alumina and potash, or of alumina and soda.

The shale is generally built up with layers of brushwood, and of clay that has been once burnt and exposed to the weather for at least a year, into heaps about 18 ft. high, 40 ft. long and 30 ft. wide. The heap is from time to time cut out on one side to supply the leaching tanks and on the other a fresh set of layers of brushwood, alum shale and red clay, reaching up to the top of the heap, is added after the previous set has been nearly completely

urnt. The brush wood is usually twigs of *tilchhi* (*Tamarix articulata*) and it is laid from 6 to 12 inches thick; the shale layer is from 3 to 6 inches thick, a little water being sprinkled on the shale beforehand for the prevention of too rapid a burning and the facilitation of the action of sulphur dioxide on the clay; the red clay is nothing but shale at least once roasted, used, dumped and allowed to weather for a year or two as to permit of any exhausted pyrites being slowly and spontaneously oxidised. This, when mixed with fresh shale in the roasting, offers a proportionately large amount of clay for absorbing some of the sulphurous fumes from the fresh shale, which would otherwise escape into the air.

This red clay after being once used, should become practically worthless, but as it is mixed up at each roasting with fresh shale it is impossible to discard it separately. The lumps grow abnormally large and are not protected from the rain which is allowed to wash away some of the results of slow oxidation. During the roasting the sulphate of iron has been decomposed and the sulphuric acid liberated has entered into combination with the alumina, forming a soluble sulphate which has now to be removed from the earthy ingredients of the calcined shale. This is accomplished by lixiviation with water.

LIXIVIATION.

This process, however, is somewhat complicated. The roasted shale is steeped in water for two days in tanks lined with a mixture of re-burnt wood-ashes, lime, and cowdung. In the course of these couple of days the mass in the tanks is stirred carefully twice and then the liquor is run into a settling tank, where it

gradually heated till all the nitrate of copper is decomposed, which may be known by taking a little of the salt, dissolving in water, and adding excess of ammonia; if copper be still present, the solution will have a blue tint. When all the copper is thus rendered insoluble, the fused mass is dissolved in distilled water, evaporated and crystallised.

The process of manufacture follows:—

Refined silver, 3 oz., pure nitric acid, 4 fl. oz.; distilled water, 5 fl. oz., mix in a glass flask, and apply gentle heat until the metal is dissolved; transfer the solution to a porcelain dish, decanting it off a heavy black powder which appears at the bottom of the flask. Having evaporated it to dryness, raise the heat (in a dark room) until the mass liquefies; then pour it into moulds furnished with cylindrical cavities of the size of a goose-quill, and which admit of being opened by a hinge; preserve the concentrated salt in well-stoppered bottles, impervious to light. This is then known as lunar caustic.

To obtain silver nitrate from solution of an alloy of silver and copper a portion of the solution is treated with potassium hydrate; this precipitates silver oxide, together with a small portion of copper oxide. This is washed and then boiled with the remainder of the solution, when any copper nitrate present is precipitated as copper oxide, and an equivalent of silver dissolved in its place.

Pure nitrate of silver, whether crystallised or fused, should be entirely soluble in water, yielding a colourless solution, from which metallic silver is precipitated by a piece of bright copper; both forms are originally white, but are darkened by exposure to light and contact with organic matter.

WHITE LEAD.

White lead is the oldest of all white paints. It has been the exclusive basis of all oil paints.. It also possesses a very pretty white colour. This is a distinctive property as quite a range of shades can be obtained by suitable mixtures with other paints.

DUTCH PROCESS.

In the manufacture of white lead, metallic lead cast into rough gratings is placed into earthenware pots by means of which the lead is subjected to the action of vinegar. The pots containing the lead are placed in a row and boards are put over them; then $3\frac{1}{2}$ ft. of spent tan bark is placed on the top of them, then another row of pots and bark, and so on till the room is full. For three months, or ninety days, the lead remains there; it is then taken out.

The greater part of the lead is acted upon by the vinegar and carbonic acid from fermenting tan bark and is turned to carbonate of lead. It is then crushed up in a mill and passed through a very fine sieve. This fine sieve will only allow the carbonised lead to pass through, not the bits of blue uncorroded lead. It is now mixed with water in a large tank fitted with agitators, and as it leaves this tank it is ground between very hard stones. After being ground, it is floated successively over five or six troughs of water, so that impurities may settle, and nothing but the pure carbonate of lead can pass the last trough. It is then dried. The final process is to grind up the pure carbonate of lead with oil, to make the lead as the painter receives it to work with. When it leaves the pan it is perfectly fine; any further grinding is only to perfectly incorporate the oil with the colour.

The white lead produced by the Dutch process is not of constant composition, varying between 60 to 80 per cent. of lead carbonate and 17 to 38 per cent. lead hydroxide.

ENGLISH PROCESS.

The English process may be adopted as follows: Mix very dilute acetic acid with litharge so as to form a rather thick paste. Spread this on leaden plates which are arranged in a closed chamber. Then pass a current of pure, well-washed carbonic acid gas into it. With the help of scrapers stir the pasty mass from time to time so that the gas may be readily absorbed. Add a fresh amount of litharge from time to time. The mass will be gradually converted into white lead, the process, being completed in $1\frac{1}{2}$ months.

ZINC OXIDE.

Zinc oxide is made by placing carbonate of zinc in a covered clay crucible, and by exposing it to a very low red heat until a portion taken from the centre of the mass ceases to effervesce on being dropped into dilute sulphuric acid. A white tasteless powder is obtained.

ZINC WHITE.

Zinc white, the anhydrous white zinc oxide, applied instead of white-lead as a pigment, is prepared by oxidising metallic zinc in fire-clay retorts, placed to the number of 8 to 18 in a reverberatory furnace. As soon as these retorts are at a bright white-heat, cakes of zinc are placed in them and the vapours of the metal on leaving the retort are brought into contact with a current of air heated to 300°C ; oxidation results and the oxide, a very loose, snow-white, flocculent material, is carried by the current

hot air into condensing chambers, and gradually deposited. The oxide thus prepared is immediately fit for use.

Another method of manufacturing zinc white is known as the American Process. The raw material employed in this case is ores of zinc. The crushed ore is intimately mixed with fine anthracite and charged in special furnaces upon perforated gratebars. These furnaces are built on the plan of a fire box and are provided with an undergrate blast. The furnace chamber is closed during operation and is opened only during the process of charging. These furnaces are placed back to back in 'blocks' and each block discharges the products of combustion and the oxide fume into sheet iron flues which convey them into the collecting system. While charging and discharging, a damper over the furnace is kept closed to prevent contamination of the oxide in the collecting system. The furnace gases are drawn through the flues by a suction fan placed in the line between the furnaces and the collecting system, the fan serving also to deliver the gases and fume into the latter. The oxide together with the gases from the furnace, in their passage to the collecting system are thoroughly cooled.

The collecting system consists of a series of bags suspended vertically, a system of horizontal pipes, which are connected to the flue. Their mesh is such that it readily permits the escape of the gases, but retains oxide. From these bags the latter is removed from time to time, properly graded, bolted through silk bolting cloth, and packed by machinery into barrels containing 300 pounds of the oxide.

LIME.

Lime is the protoxide of calcium, an earthy substance of a white colour, moderately hard but can easily be reduc-

ed to powder, either by sprinkling it with water or by trituration. On a large scale it is prepared by calcining chalk, marble or lime stone. The lime-kilns are usually of the form of an inverted cone and are packed with alternate layers of limestone and fuel, and the burnt lime raked out from the bottom. The lime thus obtained is a pale yellow powder, combining eagerly with water and crumbling to a light white powder—slaked lime—with the evolution of much heat.

Lime is extensively used in building as mortar and in fertilising land. It is also used as a medicine and a disinfectant.

CALCIUM CARBIDE.

Calcium carbide is an important article of great commercial value. A mixture of lime and carbon in some definite proportions on being fused produces carbide of calcium. The chief difficulty on the way of starting its manufacture is that it requires a special type of electrical furnace to bring out the chemical reaction between the substances. Ordinary type of furnace does not produce so much heat which is needed for the purpose.

The choice of the raw materials for calcium carbide manufacture requires care as otherwise the process may be dangerous or the resulting product may be contaminated with undesirable matter. The presence of magnesia interferes with the carbide formation; any phosphorus may give rise to phosphoretted hydrogen if the carbide is utilised for the production of acetylene; whilst if the coal used contains much mineral matter the end-product may be of bad quality.

The raw materials are coarsely pulverised and mixed in proportions of 95 parts of lime to 68 parts coke. In

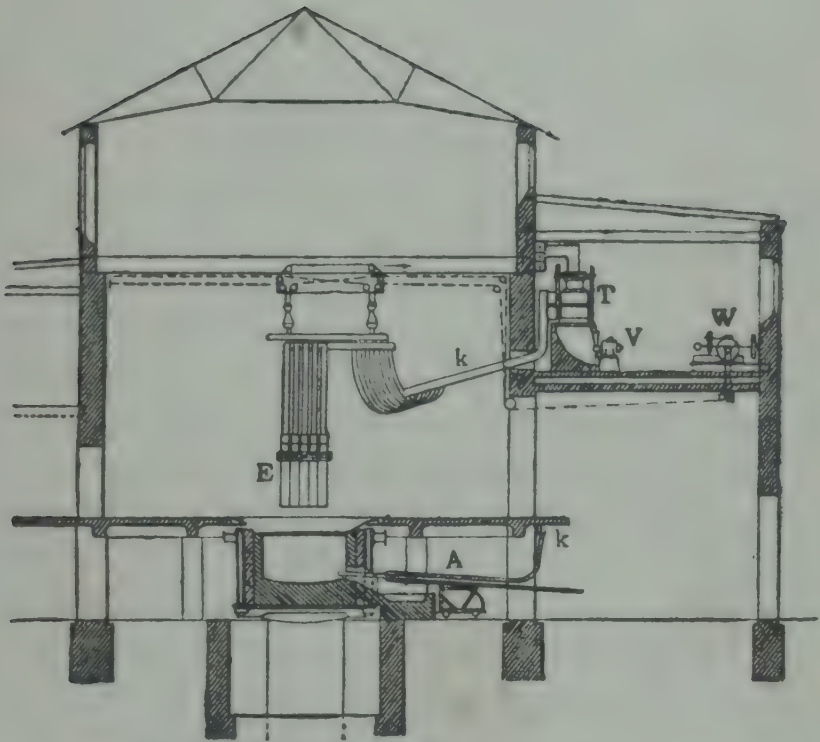


FIG. 28, MODERN CALCIUM CARBIDE FURNACE.



Architectural drawing of a building, showing a two-story structure with a gabled roof and a porch.

ory, 1 ton of carbide is obtained from 1.79 tons of mixture of lime and coke. The mixture is fed into the furnace, the form of small lumps.

Since under the conditions of the preparation the carbide is liquid, two possibilities present themselves: (1) it is possible to let the furnace contents solidify at the end of the run, or (2) to run off the liquid carbide from the furnace as it is formed. The furnaces used for the first process are termed ingot furnaces, whilst the second method is carried out by means of tapping furnaces.

INGOT FURNACE.

One of the most effective types of ingot furnace is that devised by *Wilson*. The actual furnace is a sheet-iron box about 6 feet high, mounted on wheels so that it can travel along a railway. The two graphite electrodes are mounted vertically over the line of rails and can be lowered into the box when it is in the proper position. After the contents of one box have been treated, the electrodes are raised; the box is rolled away; and another box is brought under the electrodes in its turn. In this way charges can be treated in succession by the same pair of electrodes; and no time is wasted in cooling the product. The furnace charge consists of burnt lime and anthracite or coke crushed to pieces about a quarter of an inch in diameter. Powdered material does not give such good results as granulated particles do. The charge is introduced down chutes and is kept on a level about 2 feet above the arc. It is stirred up at intervals to facilitate the escape of gases. The weight of the charge is about 10 cwt. and from this some 800 lbs. of commercial carbide is obtained.

Other types of ingot furnace have no truck, but instead the bottom of the furnace opens outwards so as to allow

the carbide to drop through. There is also the *Horry* type, in which the rotary principle is employed; so that once the calcium carbide is formed it is removed into a cooler region, by the slow revolution of the furnace, whilst the arc plays upon fresh raw material.

TAPPING FURNACE.

Turning now to the tapping furnaces, these are furnished with a large vertical electrode, about 8 feet long, composed of rods held in a circular holder and having carbon paste rammed into the interstices of the mass. The furnace is permanent, and is provided with a vent through which the molten carbide is drawn off (or "tapped") as it is formed.

The type of furnace generally used—employed in this case is shown in Figure 28. It is made of fire brick and lined with carbon; it is designed for 3000 to 4000 kilowatts. The iron bottom of the furnace connects with the carbon lining of the bottom, to form an electrode, and the other electrode is suspended so that it hangs free within the hearth. The fused carbide forms a pool under the electrode, which is raised or lowered as need be by the hoist. The furnace is tapped at intervals, by means of special arc, sprung at the end of the pointed tapping electrode by which a hole can be melted through the furnace wall in a few minutes.

For a short time previous to tapping, no fresh charge is introduced and the fused carbide in the furnace forms a thin, liquid bath. The charge itself serves to protect the fire-brick walls from the intense heat of the arc.

The molten carbide is allowed to cool in cast-iron trays, where it forms slabs about 6 inches thick, which are afterwards broken up and stored in air-tight steel drums.

Calcium carbide when pure, is white, but commercial carbide is dark grey or bronze coloured owing to the presence of impurities. It is sold packed in tin cans to protect from deterioration by exposure to the moisture of the atmosphere. It is used for generating acetylene for illuminating purposes. In recent times it has been employed for the fixation of nitrogen from the atmosphere.

RED LEAD.

Red lead is produced by heating litharge in the air at a temperature of about 480°C . The process of manufacture may be divided into two stages:—(1) the conversion of metallic lead into massicot. This is known as crossing, (2) the transformation of this product into red lead.

DROSSING.

The pig lead is thrown on the bed of a reverberatory furnace and raised to a dull red heat i.e. just above the melting point of lead. 335°C or 635°F . The molten lead thus obtained is stirred from time to time with long iron rakes so as to expose fresh surfaces of lead to oxidising influence of the air, and as fast as the yellow scum forms on the surface of the lead it is raked to the back of the furnace. Care must be taken not to raise the temperature too high, otherwise the scum or dross will be converted into the red litharge which cannot be turned into red lead. The operation takes from 12 to 24 hours, according to the size of the charge.

The yellow coloured massicot is then raked out and thrown under water and levigated. By the means the unchanged lead is removed, and the fine yellowish lead monoxide is dried ready for the next operation.

FROM MASSICOT TO RED LEAD.

The yellow massicot is next introduced into the same furnace again and heated at a low red heat in the presence of a large amount of air to ensure perfect oxidation. Care must be taken at this stage not to allow the temperature to get too high, otherwise the red lead would be decomposed. Instead of reverberatory furnace small scale manufacturers can use muffle furnace and heat it to a low heat as before. The operation takes about 12-15 hours. Towards the end of it samples are taken out from time to time and examined to see if the colour is upto standard. When this point is reached the contents of the furnace are immediately raked out. The red lead is then finally ground and is ready for use as a pigment.

The red lead should be of a good bright colour, fine in texture. It must not contain any added matter such as litharge, barytes, clay, whiting, etc. It must contain not less than 90 per cent. true red lead content. It must contain not more than 0.5 p.c. of matter soluble in water.

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WEIGHTS AND MEASURES.

1 gram = the weight of 1 cubic centimetre (c.c.) of water at 4°C.

1 grain = 0.0648 gram.

× 1 oz. avoirdupois = 453.593 grams.

1 litre = 1 cubic decimetre = 35.214 fl. oz.

1 gallon = 4.54596 litres.



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